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BY

LAWRENCE ADDICKS

CONSULTING ENGINEER, NEW YORK CITY

BAHI

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To

M. M. A.

PREFACE

Electrolytic copper refining was for so many years conducted under conditions of strict commercial secrecy that but little has been published regarding the principles of operation, as distinct from descriptions of individual plants.

This little book comprises a series of articles, each dealing with one of the problems of refining, which originally appeared in Chemical and Metallurgical Engineering.

Whatever of value it may contain is due to the fact that it is almost entirely a record of personal experience in a field where but little literature is available.

LAWRENCE ADDICKS.

NEW YORK,
December, 1920.

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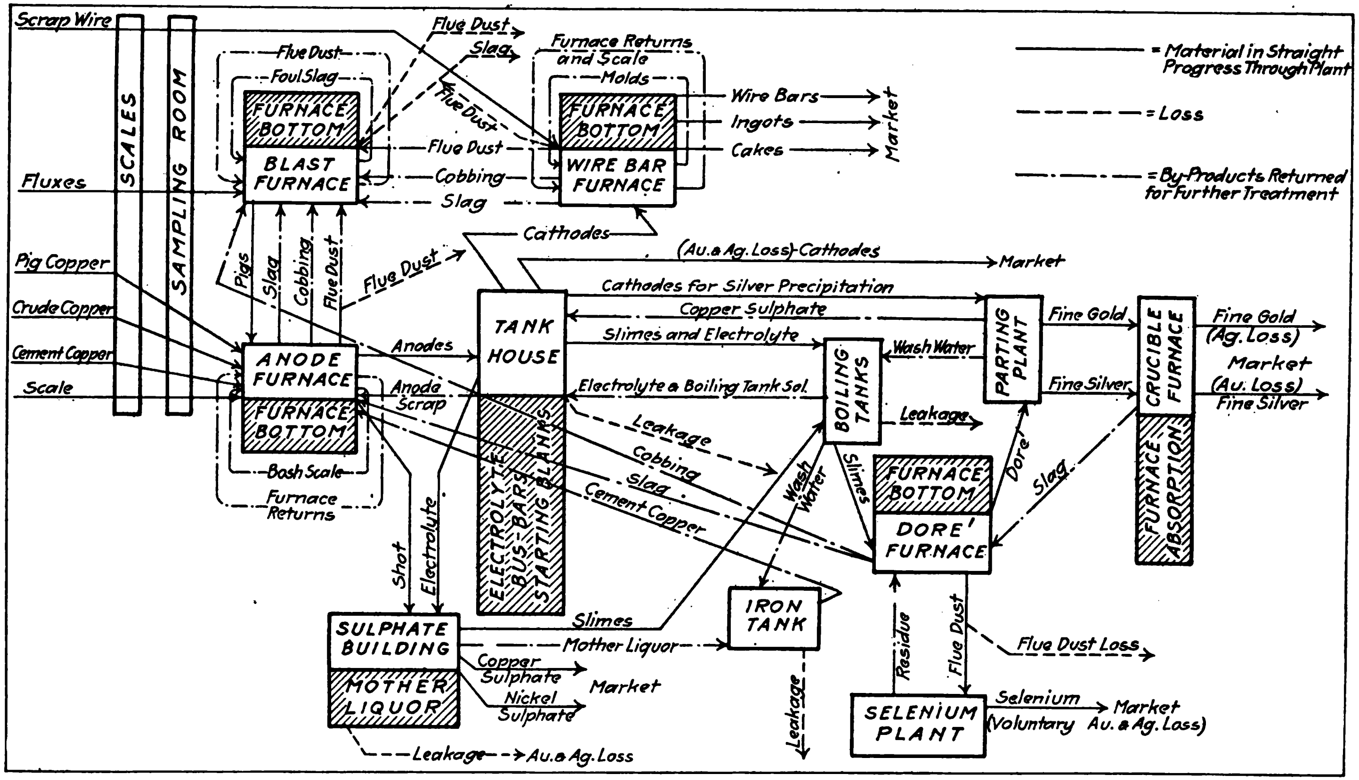

Scrap Wire
Fluxes
Pig Copper
Crude Copper
Cement Copper
Scale
SCALES
SAMPLING ROOM
Flue Dust
Foul Slag
FURNACE BOTTOM
BLAST FURNACE
Pigs
Slag
Cobbing
Flue Dust
Flue Dust
Slag
Flue Dust
Flue Dust
Cobbing
Slag
Furnace Returns and Scale
Molds
FURNACE BOTTOM
WIRE BAR FURNACE
Wire Bars
Ingots
Cakes
Market
Cathodes
(Au. & Ag. Loss)-Cathodes
Market
Flue Dust
ANODE FURNACE
FURNACE BOTTOM
Bosh Scale
Furnace Returns
Anodes
Anode Scrap
TANK HOUSE
ELECTROLYTE BUS-BARS STARTING BLANKS
Cathodes for Silver Precipitation
Copper Sulphate
Slimes and Electrolyte
Electrolyte & Boiling Tank Sol.
Leakage
Cobbing
Slag
Cement Copper
BOILING TANKS
Wash Water
Leakage
Wash Water
Slimes
PARTING PLANT
Fine Gold
Fine Silver
Dore'
Slag
CRUCIBLE FURNACE
ABSORPTION FURNACE
Fine Gold (Ag. Loss)
Market
(Au. Loss) Fine Silver
FURNACE BOTTOM
DORE' FURNACE
Shot
Electrolyte
SULPHATE BUILDING
MOTHER LIQUOR
Slimes
Mother Liquor
Copper Sulphate
Nickel Sulphate
Market
Leakage
Au. & Ag. Loss
IRON TANK
Leakage
Residue
Flue Dust
Flue Dust Loss
SELENIUM PLANT
Selenium
Market (Voluntary Au. & Ag. Loss)
= Material in Straight Progress Through Plant
= Loss
= By-Products Returned for Further Treatment

FIG. 1.—Flow sheet of a copper refinery.

COPPER REFINING

CHAPTER I

METAL LOSSES

It is only recently that the general question of metal losses in metallurgical practice has begun to receive anything like the attention it deserves. In any scheme of metallurgical treatment it is always easy to recover say 50 per cent of the value in an ore by some simple direct process. Then improvements are made which will bring the total recovery up to perhaps 65 per cent, but this additional 15 per cent has cost more per unit than the first 50 units. The process gradually develops in this way until the additional complexity brings the operating cost up to a point where

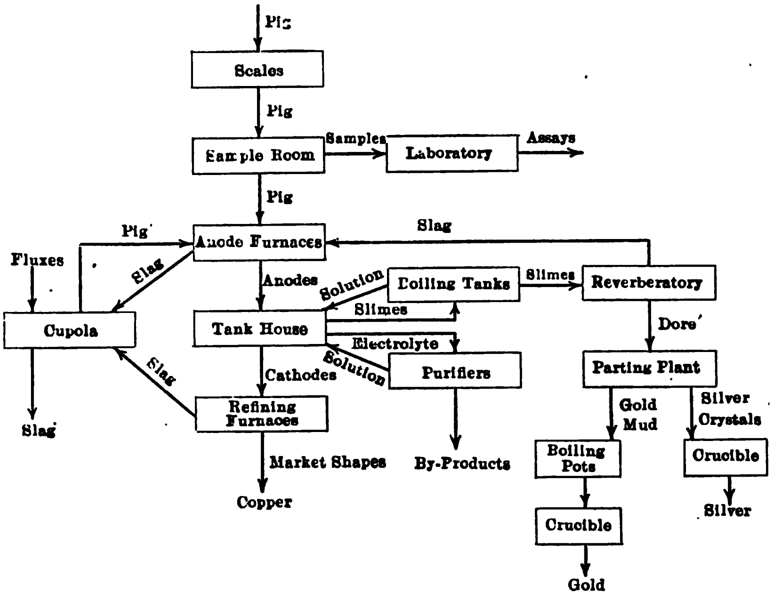

Pig
Scales
Pig
Sample Room
Samples
Laboratory
Assays
Pig
Pig
Anode Furnaces
Slag
Fluxes
Slag
Anodes
Solution
Coiling Tanks
Slimes
Reverberatory
Slimes
Cupola
Tank House
Electrolyte
Dore'
Solution
Cathodes
Purifiers
Parting Plant
Slag
Gold Mud
Silver Crystals
Refining Furnaces
Slag
Market Shapes
By-Products
Boiling Pots
Crucible
Copper
Silver
Crucible
Gold

FIG. 2.—Diagram of process.

further recovery would cost more than the value of the additional metal recovered. It is also soon found that a high recovery process can profitably treat a leaner ore, and this adds another variable to the most economical efficiency equation.

Nor is the study of the various sources of metal loss a simple analysis of slag and stack losses, although these are among the largest and most obvious sources. While we are now considering copper refining, or the separation of blister copper into fine copper, gold and silver, the method of examination will apply equally well to any other metallurgical process.

Figure 1 gives a flow sheet of the process under consideration and in Fig. 2 this flow sheet is reduced to its simplest terms. The sources of loss to be considered may be classified as follows:

A. *Weighing:*
    a. Incoming blister copper.
    b. Outgoing copper.
    c. Outgoing silver and gold.
B. *Sampling:*
    a. Moisture.
    b. Errors in method.
    c. Salting.
C. *Assaying:*
    a. Assay methods.
    b. Splitting limits.
    c. Assay errors.
D. *Slags:*
    Cupola slag.
E. *Stack Losses:*
    a. Anode furnace stacks.
    b. Refining furnace stacks.
    c. Silver refinery stacks.
    d. Cupola stack.
F. *Process Losses*
    a. Silver and gold in outgoing copper.
    b. Silver in outgoing gold.
    c. Gold in outgoing silver.
    d. Minor losses.
    e. Process margins.

G. Handling Losses:

- a. Wind losses.
- b. Theft.
- c. Solution losses.
- d. Soil losses.
- e. Slimes losses.

A. WEIGHING

Scales are about the most precise pieces of physical apparatus we have. In the laboratory when we get a sensitiveness of 0.01 mg. with a capacity of 1 gram, we are working to 0.001 per cent and even lesser ratios are obtainable. In large-capacity scales the best precision obtainable is about 0.01 per cent; that is, if we want to be sure of the nearest pound we must not use drafts exceeding 10,000 lb. Using a 200,000-lb. railroad scale which to-day can be made distinctly responsive to a 20-lb. change in load gives the same precision, but does not equally satisfy a customer who places great stress on individual pounds.

It is, therefore, customary to weigh outgoing copper in 5-ton drafts under such conditions that the refineries have been able to stand upon their weights as final, provided the consignee agrees with the count of pieces. In order to accomplish this, two platform scales are placed in tandem, separate weighers taking readings and comparing figures before passing a lot. These scales are either of the overhung type where the knife edges are overhead and always in sight, or baby railroad scales. The latter are to be preferred as they are free from the obstructions above the floor line and it is possible to arrange the live platform so that an oncoming car divides the shock between two pairs of knife edges, greatly saving wear.

The standard of weight is furnished by the certification of the U. S. Bureau of Standards of a 50-lb. brass weight as a "Class B or Working Standard." Against this are checked a sufficient number of 50-lb. cast iron weights, adjustable by lead shot, to make up a full-scale load.

These weights are not suitable for every-day use as they afford a great surface for the condensation of moisture, collection of dirt, etc., so a test car loaded with very heavy cast iron weights is checked against them every two or three weeks and this test car is used for daily checks on the merchant scales. In this way it is quite practicable to maintain the desired precision of 1 lb. in 10,000. As identical methods are used for weighing incoming blister and outgoing wirebars there is but small chance of tracing any copper losses to scales in a modern plant.

In weighing the silver and gold the situation is somewhat different. The incoming silver and gold are weighed as blister copper as outlined above, while the outgoing shipments are weighed as bullion. As the gold is always shipped to a U. S. Assay Office whose weights are final, we again come to government standards and have automatically a weekly check against the refinery bullion balance. In one of the large refineries a year's returns showed a difference of but 0.0015 per cent. As a bullion balance is furnished with a set of weights instead of a sliding poise, it is comparatively easy to make mistakes in reading. To lessen this danger it is well to provide a direct-reading spring balance upon which a check to the nearest ounce can rapidly be made.

One of the most fruitful sources of error in weighing lies in the inaccurate taring of cars. Slight differences are bound to occur daily as the oil works out of the bearings but this is not serious. Wear and tear gradually lowers the weight of a car and it should be tared at least every ten days, the weight and date being painted on each side of the car and the rule adopted not to use any out-of-date cars. Similarly a car sent to the shop for repairs should have the weight painted out.

B. SAMPLING

a. Moisture.—It is generally assumed that copper carries no moisture. This question was first raised a good many years ago when some blister copper from Australia which had been more or less immersed in bilge water in transit was found to carry about 0.5 per cent of moisture. Pig copper is quite porous and a quart of water poured on the face of a pig will vanish as if absorbed by blotting paper. The same question arises when smelters quench converter bars in boshes. About all that can be done in such cases is to make careful tests in a drying oven on certain pigs and apply the correction found to the lots represented. It is evident that a very serious source of loss may pass unsuspected if this is not watched, as the refinery will be accounting for water as copper, silver and gold.

Then we have the question of weighing material that has been exposed to inclement weather. This should never be done, but sometimes it has to be done in order to save large delays, and it is then necessary to impose an arbitrary allowance by agreement. The weighing of hot wirebars does not seem to cause any appreciable error, the rising air currents being negligible. Weighing in the wind is more serious and scales should always be well protected.

b. Errors in Sampling Method.—The silver and gold contents in a ton of blister copper may be worth anywhere from $10 to $500, although, fortunately for the refiner's peace of mind, there are very few very rich bullions. One hundred dollars per ton would be an ordinary figure, however. It can readily be seen that a small error in determining the true metal contents of blister copper would have an alarming effect upon the refiner's profits. A great deal of experimental work has therefore been done in developing standard sampling methods.

Blister copper usually runs 98 per cent to 99 per cent copper, the bessemerizing of matte having reduced the impurities to small values. The molten blister is poured into open molds and whether or not the copper is afterwards quenched in water it is always allowed to set before being removed from the mold. The pig therefore cools most rapidly on the sides and bottom, the heat being absorbed by the metal mold, and the last spot to cool is the upper central portion. The silver and gold and other impurities form a complicated series of solid solutions and eutectics with the copper, the richest portion in precious-metal values being the last to solidify.

It is evident that any system of sampling must bear this in mind. Theoretically this would require that when a sampling templet is laid out with a series of holes for drilling, these should be arranged to straddle and not pierce the center line of the pig, as no compensating holes can be drilled in the absolute edge of the piece. Practically this does not seem of great importance as experiments have shown that the richest zone often lies in a ring around the center rather than in the actual center, but it is wise to follow the theoretically proper practice as different combinations of impurities produce quite different results.

The old-style pig, shaped more or less like a loaf of bread, is now no longer in use except in South America where purchases of bullion are generally made by lot at auction rather than by contract. These old pigs were 6 in. thick and the segregation defied accurate sampling at a reasonable cost. The refineries have succeeded in introducing a bar about 18 by 27 in., 2½ or 3 in. thick, weighing about 300 lb., with just sufficient draft to facilitate removal from the mold and preferably unquenched. This readily yields an accurate sample, stacks well and is heavy enough to be an economical unit in handling.

The Japanese still make very small pigs weighing some 50 lb. each. These cause heavy sampling and handling costs and are therefore undesirable. Once in a long while copper comes from some out-of-the-way corner of the world which has been cast in pots and these cases call for considerable knowledge and ingenuity on the part of those in charge of the sampling.

A number of other precautions must be taken to secure an accurate sample of pig copper. There must be a sufficient number of holes in the templet—that is, one hole must not represent too large an area, otherwise experience has shown that the sample will be too high. In fact, careless sampling will generally give results on the high side. On the standard pig a quarter templet with forty-eight ½-in. holes is generally used; this gives an area of about 2½ sq. in. per hole. Each hole is in the center of a rectangle, arranged so that forty-eight such rectangles would just cover one-quarter of the area of a pig. The hole is drilled completely through the pig, each successive pig sample being marked at the next hole in rotation on the templet. In these days of large converter pours it is seldom necessary to drill every pig, one in three, four or even five being sufficient.

It must be realized that there is always more or less dirt on the surface of a pig and also that the set side has an oxide film which may run quite different in values from the body of the metal. It has been proved that decidedly different samples are obtained from a lot depending upon whether the pigs were drilled face up or face down, and further that while for a given brand of pig these differences are generally consistently in one direction, some brands would be the reverse of others. This dilemma has been met by using the so-called top and bottom method. Originally every other pig was turned bottom up, but it was found equally satisfactory to drill every other lot bottom up. No water or lubricant should be used on the drill as this will tend to oxidize the hot drillings.

A splash sample taken at the smelter by collecting a fraction of the converter pour as shot in water will always show high metal values as against the refinery as such a sample is automatically freed of dirt and slag. For a long time the smelters felt that their splash samples were correct and that the refineries' samples low, but it has been shown that a properly taken sample at the converter, using no water, can be made to check drill samples on the pig.

Enough has been said to show that sampling methods are a matter of the highest importance in any study of the sources of metal loss, as the refiner has to pay on the values shown by the sample whether or not they exist in the pig.

c. Salting.—The contamination of a sample during preparation may cause serious errors and consequent apparent metal losses. Nowadays this is seldom done deliberately, although the large laboratories generally have one or two interesting stock tales of this character. It may easily be done unconsciously, however, if silver-refinery slags, doré samples, etc., are handled in the same department as incoming pig copper. The only sure way is absolutely to separate such different classes of work.

C. ASSAYING

a. Assay Methods.—In the early days an assay method was supposed to represent the process to be used and the assay value was admittedly lower than the true contents by an amount approximately equal to the expected loss in treatment. In other words, the assay value was the recoverable value. To-day the tendency is to adopt methods which will give the highest result compatible with reliability but which still do not in all cases give full contents. The electrolytic assay for copper does give full value; in fact the chief danger in the handling of this method is that some impurities may be deposited on the cathode and weighed up as copper, to the disadvantage of the refiner.

The so-called uncorrected combination assay for silver in which the bullion is dissolved in nitric acid, the silver precipitated as chloride which in turn is scorified to gather the silver (and gold) into a lead button, the button being cupeled and the resultant bead weighed as silver plus gold, does not give full value of silver by from 2 to 3 per cent. The loss is due to values in scorifier slags, to cupel absorption and to volatilization. The main argument for this method is that when conscientiously run it will duplicate results very closely while there is at present no really satisfactory method of determining the absolute silver contents of foul bullion.

Skill is required in maintaining the proper temperature when cupeling; it must be hot enough to make the button "blick" at the finish, or it is not pure and other elements are weighed as silver; on the other hand it must be cool enough to show "feather" litharge around the edge of the cupel when finished, or the volatilization loss will be excessive.

Mismanagement in the laboratory may easily affect the apparent or financial metal losses. In some cases the "corrected" assay is used, where the losses in scorifier slags and cupels are determined and added, bringing the recovery up to about 99 per cent. Nothing is gained in accuracy and when once the particular bullion is known, the amounts of these losses are very constant and can just as well be allowed for arbitrarily in the refining terms, avoiding the expense and delay of determining daily corrections.

There is no practical way of ascertaining the volatilization loss except by running "proofs" made up with known quantities of silver. With high-grade doré and similar pure material this is satisfactory, but when various impurities are present, they affect the volatilization and a true proof would be a very complicated affair.

In the case of gold the fire assay, where the bullion is scorified direct to a lead button, is used as it gives a higher value than the gold parted from the silver in the combination assay, due probably to filter losses and the oxidation of some gold when dissolving the bullion in nitric acid in the latter method. This gives a return of about 99.6 per cent in the uncorrected assay. The corrected gold assay is very close to full value. The so-called mercury or sulphuric acid method is an equivalent of the fire assay.

b. Splitting Limits.—Were assays absolutely accurate and all laboratories equally reliable, the question of splitting limits would not enter into a discussion of metal losses. As such is not the case it is necessary to agree upon some reasonably allowable difference between buyer and seller within which assays shall be averaged or "split" and beyond which an umpire assayer shall be called upon.

In order to guard against either dishonesty or carelessness several simple precautions should be taken. In the first place assays should be exchanged simultaneously by mail; then all "reassays" to avoid umpires should be forbidden; finally, splitting limits should be made as close as possible. Sometimes the splitting limits are made very close, such as 0.1 per cent for copper, for example, and then only such umpires undertaken as may be necessary to bring the average results for ten consecutive lots within splitting distance.

The umpire should be considered simply as a substitute for one assayer, not as a source of authority. When two assays fall too far apart, the assumption is that one is incorrect and the umpire will determine which one it is. His result should therefore be averaged with the nearest original result unless it is above the higher or below the lower by more than the splitting limit, in which case the sample is pronounced uneven and the two original assays averaged for settlement.

In many cases where wild umpires are reported the trouble with the sample can be rectified by screening out the fines in the sample and then making up a portion for assay with just the proper proportion of fines, the more impure parts of the alloy having been brittle and pulverized under the drill.

It is also well to have two or three competent umpire chemists agreed upon, assigning umpires, as they become necessary, in rotation. This tends to check any inaccuracies in the umpire laboratory.

c. **Assay Errors.**—Assays are subject to three sources of error: (1) those of method; (2) those of procedure; (3) those of calculation, or clerical errors. The first has already been dealt with and may be classed as a voluntary error; the second may be due to carelessness, inaccurate apparatus, such as scale weights or burettes, or impure reagents; the third is more serious than might be imagined and constant vigilance is necessary. Perhaps the most common clerical error is that of reporting double or half the proper value in silver and gold determinations, due to failure to note the fraction of an assay ton taken for assay.

D. SLAGS

We have now to pass from the apparent losses due to inaccurate accounting for values in the incoming bullion, to the actual metallurgical losses, and the first of these is the loss in the cupola slag. The anode and refining furnace operations produce a certain amount of slag due to the reaction between the metallic oxides formed during scorification in the furnace and silica and other oxides present in the furnace walls and hearth, or introduced as coal ashes blown over from the fire box, or as clay used in luting up the doors, fettling, etc.

In the old days of small furnaces constructed entirely of siliceous material, from 3 to 4 per cent of the weight of the charge was made in slag. In the large modern furnaces constructed partly or wholly of basic or neutral material and with much better fuel economy, the slag made is below 1 per cent.

Theoretically the slag should be a very small item. After a charge is melted air is blown in sufficient to oxidize part of the copper. This cuprous oxide in turn displaces the impurities by oxidizing them and sending them into the slag. The cuprous oxide is soluble to a certain extent in the molten copper and were no acids present it would be theoretically possible to skim off simply these impurities with a little mechanically entangled copper. The actual slags made run about 45 per cent copper and must be treated in a blast furnace with fluxes such as iron oxide and limestone to make black copper unless a smelting plant is connected with the refinery.

If some sulphur is introduced into this charge a low-grade product running about 94 per cent copper may be made with a slag running below 1 per cent in copper, but this gives a high operating cost in the anode furnace.

If a high-grade black copper is made it is very difficult to get a slag below 2 per cent in copper. Taking a final cupola slag of 36 per cent silica and neglecting the small quantity of silica introduced by the basic fluxes, this means that every ton of silica which is allowed to find its way into the refining furnace slags carries away from 56 to 112 lb. of copper in cupola slag aside from the stack loss in this operation. It is evident therefore that this great source of loss is worthy of the most careful study, to the end that the least possible amount of slag be made at the reverberatories.

E. STACK LOSSES

a. Anode Furnace Stacks.

b. Refining Furnace Stacks.

Not a great deal is known about these losses. The recoveries in flue dust from waste-heat boilers installed in anode furnaces show some 0.07 per cent of the copper treated, rather more of the silver and less of the gold. On the other hand, bag-house tests on the gases escaping from a high direct stack have shown less than this amount. The composition of the bullion under treatment has doubtless much to do with these losses, as the recoveries on furnaces treating cathodes are much less, due partly to less working of the molten charges and partly to the absence of volatile impurities which always promote metal losses.

c. Silver Refinery Stacks.—The anode slimes consist of the insoluble impurities contained in the anode and run 30 per cent to 40 per cent in silver. The copper is mostly leached out as sulphate and the slimes are then melted and subjected to a series of oxidizing operations until a high-grade doré is obtained.

In general about 1 per cent of the silver treated and about 0.1 per cent of the gold is recovered by various means in the flue system and great progress has been made in the last ten years in this practice.

Until the Cottrell system of electrostatic precipitation was successfully applied to treating these gases, the opportunities for serious undetected losses were very great and even now there is no point in a metal loss investigation which needs more careful examination.

The great difficulty is that the actual losses made are clearly discernible only after several years, as the results from single yearly inventories are always more or less clouded by anode furnace bottom absorptions which vary from year to year, and the punishment comes so long after the crime that it is very easy to be lax to the immediate benefit of apparent operating costs. Molten silver should be handled like a volatile liquid.

d. Cupola Stack.—This loss should be relatively small, as the operations are on a small scale and the charge in reasonably good physical condition. A proper dust chamber should be installed, however.

F. PROCESS LOSSES

a. Silver and Gold in Outgoing Copper.—This loss is a perfectly definite one shown by daily assays. In general the loss runs from 0.5 to 0.8 per cent of the silver and gold present in the anodes. In the case of low-grade anodes this is not serious, but when rich material is being treated this loss becomes quite an item. The loss is due to slimes adhering to the cathode and is affected by the current density, the volume of circulation of the electrolyte, and the degree of refining given in the anode furnace.

b. Silver in Outgoing Gold.—The Government does not pay for the silver in gold deposited unless the fineness is low enough to require refining. In the latter case the refining charges imposed greatly exceed the costs of refining before shipment. The net result is that any silver contents are not paid for and therefore constitute a metal loss. This loss should not exceed two or three parts per thousand.

c. Gold in Outgoing Silver.—Any gold in outgoing fine silver is, of course, a total loss. It should be possible to keep this loss down to 0.1 oz. per ton of silver.

d. Minor Losses.—These comprise values lost in any byproducts sold, such as nickel sulphate, selenium, platinum etc., and the value of assay samples sent out without credit, etc. These sources of loss are relatively unimportant but should not be overlooked.

e. Process Margins.—These are negative losses or gains due to receiving more metal than accounted for, or to shipping less, due to trade customs. In copper there is no assay margin, but there is a gain of about 0.07 per cent due to the fact that wirebar copper runs but about 99.93 per cent copper, while it is credited as 100 per cent against incoming copper received on actual contents.

In the case of silver the uncorrected combination assay allows the refiner about 2.5 per cent margin while on shipments of fine silver, although the assay used shows true contents, a fineness of 999 is considered a 100 per cent delivery. With gold there is a margin of about 0.4 per cent in the incoming bullion from the fire assay used, but no margin in the outgoing fine gold.

G. HANDLING LOSSES

a. Wind Losses.—Wind does not cause as much trouble in a refinery as in a smelter, owing to the nature of the material handled. If the atmosphere were absolutely quiet, however, it is conceivable that the fume losses from stacks would settle down within the confines of the plant. Dust collected from the roofs of the buildings is always high in grade although very small in quantity. I have a memorandum of a sample of so-called dust swept up near a refinery furnace building which ran 65.81 per cent Cu, 49.8 oz. per ton Ag and 3.41 oz. per ton Au.

b. Theft.—A refinery is always subject to losses by pilfering and a most thorough system of patrol, passes, etc., together with a policy of prosecution of all cases detected is necessary to hold this in check. Copper is a very easy metal to sell as junk and systematic carrying away of small quantities in lunch pails, etc., may run into surprising amounts. In the silver refinery it is customary to bond the employee and to have a double set of dressing rooms with different clothes for work and for outside wear, the men passing stripped before a watchman from one room to the other at change of shift. One assistance in the detection of silver and gold thefts lies in the fineness of the products. When a man offers 999 silver or 24 carat gold for sale he at once arouses suspicion.

c. Solution Losses.—Although the day has passed when electrolytes were purified by running a proportion to the sewer at regular intervals, there is still plenty of opportunity for loss in the handling of solutions.

It is very difficult to keep the electrolyte with its free sulphuric acid confined to the circulating system on account of tank leaks, overflows, etc., and it is even more difficult to build a permanent water-tight acid-proof floor under these tanks.

Some of the earlier refineries suffered severely from such losses and I know of one plant where it was possible to dig a well anywhere in the vicinity and pump out water which gave a profitable copper recovery when passed over scrap iron.

One good way to keep track of losses from this and similar sources is to keep a careful record of sulphuric acid movements in the solutions. Serious acid losses point at once to equivalent copper solution losses. In plants where waste liquors are worked up by cementation upon iron there is an additional opportunity for loss in undertreated waste liquors.

d. Soil Losses.—Where a plant is unpaved there is always more or less metallic material ground into the earth and in a smelting plant the top soil becomes in time very good ore. In a refinery there is not the same opportunity for loss owing to the nature of the material handled and such a loss should be negligible except in the case of solution losses mentioned above and that of slimes losses taken up below.

e. Slimes Losses.—Mechanical losses of slimes could, of course, be assigned to the several sub-headings preceding, but the matter is so important that a separate paragraph has been reserved for their discussion.

Slimes originate in the tank house. They are periodically sluiced down into a screening tank whence they are usually transferred by pumping to a receiving tank in the silver refinery. A certain amount is carried out in the cathodes, a matter which has already been taken up. More or less adheres to the anode scrap when it is drawn and is removed as thoroughly as possible by scrubbing or by high-pressure water-sprays before the scrap is sent to the anode furnace. Any carelessness here may result in wind and soil losses in transit or up the stack during melting.

Tank leaks in the tank house carry considerable quantities of slimes to the cellar floor. While most of these values are recovered by washing the floor, some is absorbed and the floor material has to be smelted whenever extensive repairs are made.

In the silver building the slimes of necessity get spilled around to a certain extent and as boiling operations are conducted in this department the steam makes a sort of paste with them and care must be taken that all unnecessary walking in and out of this department be avoided, and that proper means for wiping shoes be provided. The shower baths used by the workmen should drain into the general wash water system.

The very best possible floor must be provided in this building. During some changes in one of the silver refineries some old foundations yielded up an absorption of 17,000 oz. of silver and 200 oz. of gold.

The slimes before melting have the appearance of black mud and it is very hard to get workman to handle them with the care they instinctively give to the silver sponge and other metallic products produced later.

From the foregoing it will be appreciated that constant thoughtful attention in a great many directions is necessary to make a minimum metal loss. As the precautions all cost money it raises the question whether the additional saving due to them pays. The answer to this is that it is only by constant schooling in all these precautionary measures that men can be trained to be really careful when they are on their own responsibility and not under observation.

For this reason the liberal use of white paint and many other seeming extravagances are justified. The same rigid care and supervision in the weighing, sampling, and assaying is required as in the control of slag and cathode losses, and careful attention must be given on general principles to all the apparently insignificant sources of indefinite loss.

In general a well conducted refinery, operating on clean bullion and accounting for contents as shown by electrolytic assay for copper, uncorrected combination assay for silver and uncorrected fire assay for gold, should show a loss of seven or eight pounds of copper per ton, at least break even on silver and recover a small overage of gold.

CHAPTER II

METALS IN PROCESS

Most electrolytic refining processes have to compete with fire processes which are as a rule less satisfactory technically, but which turn out the product in a very much shorter time. This slow turn-over imposes heavy interest charges on account of the large investment in plant which it implies and from the necessity of financing the metals in process. The plant investment and the amount of metals locked up are closely related to the current density employed, but as the power required increases nearly as the square of the current density, a point is soon reached where the cure is worse than the disease.

TABLE 1

Metal	Normal Pre-War Market Value Dollars per lb.	Electrochemical Equivalent Grams per Ampere-hour	Quotient X 104
Iron	0.01	1.04	1
Lead	0.04	3.86	1
Zinc	0.06	1.22	5
Copper	0.15	1.19	13
Nickel	0.30	1.09	29
Silver	9.00	4.03	232
Gold	300.00	2.45	12,700

The case varies greatly with the metal under consideration, depending upon its electrochemical equivalent and market value. Some idea of this variation can be obtained from an inspection of Table 1, which takes the ratio of these two factors as a measure of the relative costs. Although this table is inexact in that it ignores voltage and other minor factors it shows how in the case of lead a handicap has been removed enabling electrolysis to compete with the best of fire processes, while gold is electrolyzed in but few plants not under Government auspices, where locked values are not of any importance.

The question is somewhat complicated by the fact that the bullion being electrolyzed is generally a mixture of two or more metals, each of which is to be recovered. The refining of blister copper carrying silver and gold will serve as an example upon which to base discussion of the general problem.

Copper refining contracts specify certain permissible elapsed times for the return of or payment for the values in the bullion to be refined, varying from 45 to 75 days for the copper and from 60 to 90 days for the silver and gold. It is evident that the earlier the metals can be put on the market the sooner their cash value can be put to earning money elsewhere and, therefore, that each day that the process locks up the values has a definite cash value. This is not greater than 6 per cent, however, as the banks consider warehouse certificates based on metals in process satisfactory collateral for loans up to a high percentage of their market value in ordinary times. Taking copper at fifteen cents a pound, the interest value of a sixty-day refining allowance is three dollars a ton, and each ton-day costs five cents, with corresponding values for the silver and gold contents. The cost of refining is made up of operating expenses, metal losses and metal interest, and it is the purpose of this chapter to examine the last.

Metals are tied up in process for three quite different reasons which might be stated as commercial, technical, and balancing. Commercial policy makes it desirable to hold incoming bullion at times before putting it into process until certain conditions are fulfilled, such as agreement of assays, or such a state of weather as shall obviate the necessity of moisture allowance when weighing; or fluctuations in the metal market may make it advantageous to go to extra operating costs to cut down what normally would be considered proper stocks in process or to delay the purchase of metals lost in process; finally it is good policy to endeavor to carry reasonable stocks of refined shapes on hand so as to be able to adjust shipments to unexpected changes in orders, steamer sailings and the like. It is quite reasonable to have 10 per cent of the total tie-up in copper due to such causes.

Then we have the values locked up for technical reasons which may be classified as metals truly in active process, metals circulating in slags, etc., metals permanently tied up in furnace bottoms, etc., and metals forever lost to be charged into operating costs as metal losses.

Finally there are the stocks of pig, anodes and cathodes which it is necesary to carry in order to insure smooth, continuous operation regardless of minor irregularities in arrival of pig or breakdowns in some parts of the process. To these the name of "balancing" metals has been given for want of a better term.

The total metals tied up are, of course, shown by the balances due customers on the metal books of the plant, but these figures give no data of value in the analysis or control of the values. It is also customary to take periodical physical inventories of metals on hand in order to determine accurately the metal losses for the preceding term. This indicates the metal tied up in each part of the plant but unfortunately in order to take a proper inventory without shutting down the process it is necessary to introduce temporarily radical changes in operation which greatly increase the tie-up. It is, therefore, necessary to rely upon a thorough understanding of the sources of locked values and of their relative importance and a constant scrutiny of conditions in order to control this important factor in the total cost of operating a copper refinery.

Classification.—Figure 3 gives a systematic classification of the sources of locked values which we shall proceed to take up item by item. The items under the heading "Commercial" may be dismissed with the arbitrary assumption of five days delay of copper, four days of silver and three days gold.

Metals in Process.—Turning next to the delays for technical reasons and taking first "metals in process," Fig. 4 gives the direct course of the metals through the process ignoring all diversions.

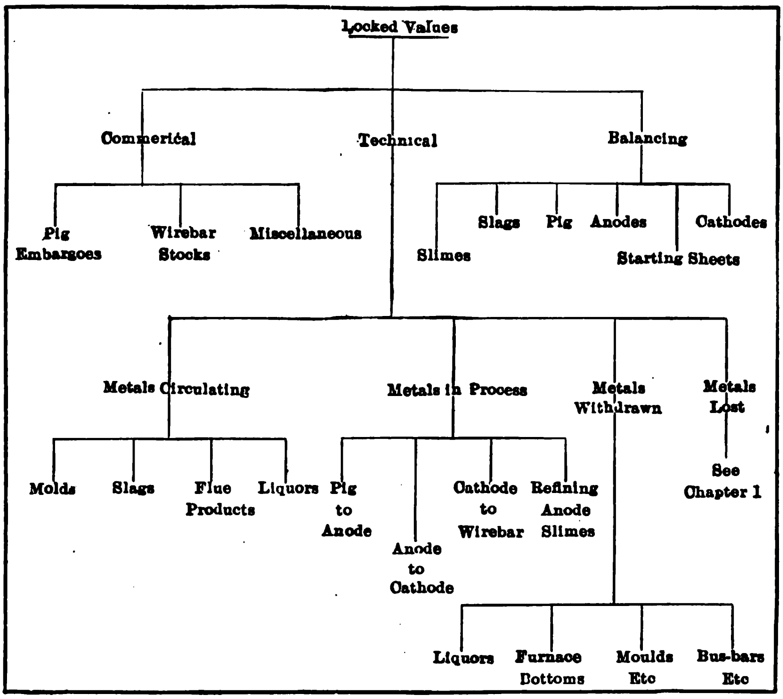

Locked Values
Commercial
Technical
Balancing
Pig Embargoes
Wirebar Stocks
Miscellaneous
Slimes
Slags
Pig
Anodes
Cathodes
Starting Sheets
Metals Circulating
Metals in Process
Metals Withdrawn
Metals Lost
Molds
Slags
Flue Products
Liquors
Pig to Anode
Anode to Cathode
Cathode to Wirebar
Refining Anode Slimes
See Chapter 1
Liquors
Furnace Bottoms
Moulds Etc
Bus-bars Etc

Fig. 3.—Analysis of sources of locked values.

The weighing, sampling, and handling of pig to the anode furnace properly occupies one day. The refining and casting into anodes is a twenty-four hour operation. In the tank house conditions vary greatly in different plants, but representative eastern practice may be taken as 14 days cathodes and 28 days anodes, making an average age of 21 days for the two sets of electrodes. The refining furnace is operated on the same basis as the anode furnace, calling for one day. Certain parts of the plant are shut down on Sundays, but this is assumed to have no effect upon the final date of delivery of refined copper.

In the silver refinery the length of time required to recover doré from the slimes will depend greatly upon the impurities present, but is not likely to be less than three days for dissolving the copper in the slimes and six days for furnacing them.

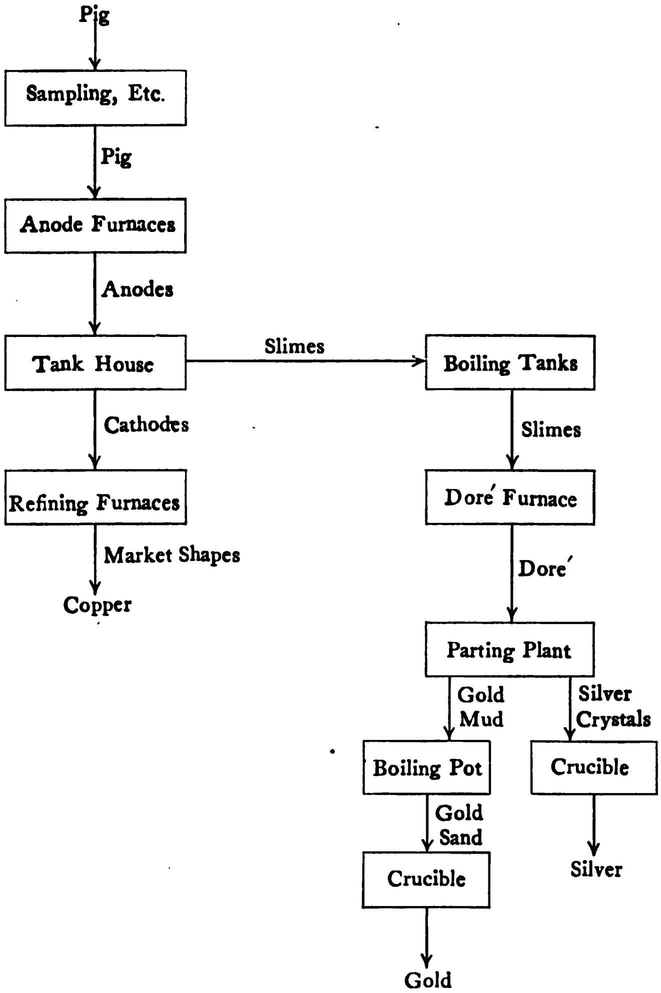

Pig
Sampling, Etc.
Pig
Anode Furnaces
Anodes
Tank House
Slimes
Boiling Tanks
Cathodes
Slimes
Refining Furnaces
Doré Furnace
Market Shapes
Copper
Doré
Parting Plant
Gold Mud
Silver Crystals
Boiling Pot
Crucible
Gold Sand
Silver
Crucible
Gold

FIG. 4.—Direct course of metals through plant.

In the parting plant, assuming electrolytic parting is used, the anodes will probably last three days and the cathode crystals be cleaned up every few hours, making an average of one and a half days. The washing and melting of the silver sponge takes but a few hours, say half a day. The gold mud would be cleaned every three days and the boiling and melting take two days.

We can now sum up the time required as shown in Table 2.

TABLE 2

	Copper	Silver	Gold
Weighing and sampling	1	1	1
Anode furnaces	1	1	1
Tank house	21	21	21
Refining furnaces	1		
Boiling slimes	..	3	3
Furnacing slimes	..	6	6
Parting doré	..	1.5	3
Melting silver	..	0.5	
Refining gold	..	..	1.5
Melting gold	..	..	0.5
Total days	24	34	37

These figures show first that but about half the time allowed for refining is required by a straight passage through the process, thereby giving the goal we should strive to approach, and second that as would be expected the slow item is the electrolysis. This time can be lessened by cutting down the age of the anodes or of the cathodes or of both. Too light an anode increases handling costs and the percentage of anode scrap made, while too light a cathode runs up disproportionate charges for making starting sheets and decreases the productive hours of the tanks, which have to be cut out while drawing copper. As before stated the power charges mount very rapidly with increasing current density.

Metals Circulating.—The sample diagram shown in Fig. 4 would become an almost undecipherable confusion of lines were it expanded to indicate every movement of circulating metals. As we proceed from pig to cathode a fraction is diverted at each stage of the process and sent back to an earlier one.

Each of the furnace processes may be illustrated by the first diagram in Fig. 5 and both the copper electrolysis and the doré parting by the second except that there are no starting sheets in electrolytic parting processes, the silver being deposited in non-adherent crystals upon a fixed carbon or silver cathode.

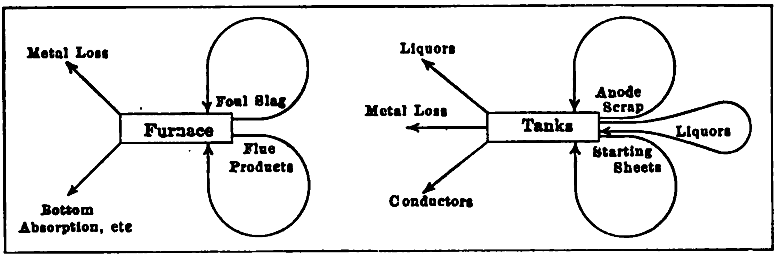


Fig. 5.—Typical metal movements.

The return arrows indicate circulating metals and the straight ones metals locked up continuously. The two cases are alike in their effect upon the process except that the former varies directly with the output while the latter are more or less constant for a given plant regardless of output. (Metals actually lost are a third case, but the quantities involved are small and are generally adjusted by systematic purchases so as to have but a negligible effect upon the time required for refining and they will be ignored.) Liquors partake of both characteristics, as a certain stock is required for starting up the plant while another quantity circulates through the purifying departments, etc.

Returning to the plan laid down in Fig. 3 we shall consider the metals circulating in slags, flue-products and liquors.

Anode Furnaces.—The first and simplest case is that presented by the anode furnaces; first because, if we ignore the small amount of values circulating in the drillings from sampling, the anode furnaces divert the first fraction from the entering pig, and simplest, because the slag and flue products made return directly to the anode furnaces themselves after being reduced to pig in a cupola, giving a single fraction to consider.

The quantity of slag made by an anode furnace varies with the purity of the pig from less than 1 per cent of the charge to several per cent. The slag itself will run from 35 to 45 per cent copper and the silver and gold slagged will be proportionately less than the copper. We shall assume that we have made 1.5 per cent of the copper contents of charge in slag running 40 per cent copper and that the silver and gold slagging ratio is 0.85 and 0.45 respectively, with copper at 1.00. In flue dust we shall recover about 0.07 per cent of the copper and say 0.1 per cent of the silver and 0.05 per cent of the gold treated. Then we have other flue products such as the cobbing from repairs, and the quantity of this also varies greatly with the character of the bullion under treatment. We shall assume it to amount to 25 per cent of the metals in the slag. Then there is a negligible amount of bad production, scale, etc., charged back next day. We have therefore as a measure of the apparent shrinkage of the values in process, ignoring actual metal losses, the figures given in Table 3.

TABLE 3.—ANODE FURNACE DIVERSIONS

	Copper	Silver	Gold
Charged to furnace	1.0000	1.0000	1.0000
Slag contents	0.0060	0.0051	0.0027
Flue dust	0.0007	0.0010	0.0005
Cobbing, etc.	0.0015	0.0013	0.0007
Total diversions	0.0082	0.0074	0.0039
Net output	0.9918	0.9926	0.9961

The actual retreatment of these by-products does not take over a day, the process being simply reduction to pig copper in a small cupola. In practice a great deal of time is lost in storage before retreatment, but this will be taken up later under "balancing" the process.

Tank House.—The tank house has three circulating items; anode scrap, starting sheets, and liquors.

Anode scrap is the part of an anode remaining after it has been eaten away by the current until but a skeleton remains hanging from the supporting lugs. These lugs generally account for from 3 to 5 per cent of the total weight of the anode and this percentage represents the lowest possible anode scrap unless lugless anodes are used as shown in Fig. 13.

In practice the scrap made varies between 7 and 20 per cent. A poorly refined anode will dissolve unevenly and cause heavy scrap, while careful filling of the "holes" caused by drawing individual anodes which work out first will lessen the final scrap made. The best policy, however, is to refine the anodes thoroughly and take no chances on disturbed current distribution in the tanks due to "lace" anodes, so that a normal percentage of scrap will be about 14 per cent of the weight of the anodes charged. This scrap is subject to a charge of 28 days in the tank house plus the time required for the anode cycle.

The starting sheets are cathodes which are deposited upon greased copper plates and stripped as a thin sheet when they are about twenty-four hours old. They are used as mother sheets upon which to build up the cathodes proper. As the cathodes are drawn in fourteen days, one twenty-eighth of the number of tanks (each copper plate or "starting blank" yields two starting sheets) must be turned over to this service. Actually a little more than this is required for the manufacture of loops by which to hang the cathodes and to allow for bad sheets and sometimes for wider spacing. The production of bad sheets will be considered negligible and one twenty-fifth, or 4 per cent, of the output will be considered to be in starting sheets which have been set back two days, one day depositing and one for attaching loops, etc., by this diversion.

The copper tied up in the electrolyte comes chiefly under the head of "metals withdrawn," but a certain amount circulates between the tank house and the silver building and the tank house and the purifying department. The first of these is a small item. The slimes are pumped over to the silver building as a soup carrying perhaps 5 per cent solids, but as the slimes amount to but about one and a quarter per cent of the anodes and as the electrolyte carries but 3 per cent copper, the total copper involved in the movement is but three quarters of a per cent of the anode weight. The slimes are settled out and the liquor returned in about twenty-four hours.

The proportion of liquor required for purifying depends, of course, upon the impurities present in the anode. In the first place there is a certain amount of copper dissolved chemically from the electrodes which would cause an accumulation of copper in the electrolyte were there no compensating factors. If the anodes are very free from impurities, insoluble anode tanks must be operated to recover about 2 per cent of the cathode output in order to strike a balance.

On the other hand if nickel is present in the anodes this dissolves electrochemically but is not deposited at the cathode, so that if much is met with a condition of actual insufficiency of copper in the electrolyte may obtain, calling for the use of shot towers.

Antimony may be precipitated chemically as oxychloride and arsenic electrolytically in the insoluble anode tanks. Iron should be adequately removed in the anode furnaces. Nickel, however, accumulates and must be removed by evaporating liquors.

It will thus be seen that quite different conditions may exist at different plants or at the same plant at different times. For our case we may assume that the equivalent of 1 per cent of the copper in the anode has to be regularly removed. Practically all of the copper contents of this solution will be eliminated in the three successive sets of insoluble anode tanks through which it will be passed as a first stage in the purification and we need not follow this further. We may assume that these tanks will be cleaned once in ten days and the product sent to the cupola.

Then we have the copper in the anode slimes returned from the silver building. This amounts to about 0.20 per cent of the copper in process, or say 0.17 per cent of the anode weight. It is returned to the tank house as copper sulphate and has about a ten-day cycle.

Summarizing, we have for a unit of anode copper entering the tank house the diversions given in Table 4.

Table 4.—Diversions from Tank House

	Copper	Route
Entering	1.0000	
Anode scrap	0.1400	Anode furnaces
Starting sheets	0.0400	Tank house
Copper in slimes	0.0017	Tank house
Electrolyte in silver building	0.0075	Tank house
Electrolyte to purifiers	0.0100	Cupola
Total diversions	0.1992	
Net output	0.8008	

Refining Furnaces.—The refining furnaces are similar to the anode furnaces as regards circulating metals except in that the quantity of by-products made is smaller owing to the practical absence of impurities and that a handicap exists owing to the necessity of sending these back through the cupola to the very beginning of the process. The values assumed for the anode furnace may be scaled down as given in Table 5.

Table 5.—Diversions from Refining Furnace

	Copper	Route
Charged to furnace	1.0000	
Slag	0.0030	Cupola
Flue dust	0.0001	Cupola
Cobbing	0.0010	Cupola
Bad production	0.0100	Refining furnace
Molds	0.0200	Refining furnace
Total diversions	0.0341	
Net production	0.9659	

The bad production consists of defective castings which are charged back into the furnace next day. The molds may be considered also as returned next day, the balance of the period by their use being considered under "metals withdrawn." We are assuming that the anode furnaces use cast iron and not refined copper molds. The small amounts of silver in gold in the refining furnace by-products are ignored.

Silver Refinery.—We come next to the silver refinery. The anode slimes carry all the silver and gold, neglecting losses, and about 0.2 per cent of the copper, as already stated. For our purposes the small amount of copper entering the doré furnaces may be neglected.

The next step in the treatment of the slimes is a reverberatory smelting. The slimes are melted and tend to form three distinct layers, bullion, matte, and slag. The slag is skimmed off and the matte, if small in quantity, as it should be if the copper has been properly removed in the slimes boiling tanks, broken up by blowing. The foul bullion is then refined to high-grade doré by cupeling without the addition of lead. The final by-products are two slags, flue dust and cobbing, all of which, with the possible exception of the cobbing which may go to the cupola, after sorting out metallics, are sent to the anode furnace. We shall assume the data stated in Table 6.

TABLE 6.—DORÉ FURNACE BY-PRODUCTS

	Weight	Assay—oz. per ton	
		Silver	Gold
Slimes	2,000	12,000	100
Poor slag	300	800	1
Rich slag	500	1,200	6
Flue dust	200	1,200	1
Cobbing	40	1,200	6

The doré is sent to the electrolytic parting plant, but as there is neither anode scrap, nor starting sheets, assuming the Thum-Balbach system with horizontal electrodes is employed, the only circulating values are in the wash waters from the crystal silver and these are so small that they may be neglected here. The same is true of the slags from the crucible melting of the gold and silver.

There is, however, some circulating silver from the refining of the gold anode mud. This mud may be considered half gold and half silver, so a quantity of silver just equal to the gold output is dissolved in the boiling kettles and sent back to the slimes boiling tanks. As we have assumed slimes with 12,000 oz. per ton of silver and 100 oz. per ton of gold this represents a diversion of 0.0083 or a net output of 0.9917.

We can now build up a schedule for the reverberatory doré furnace. This is given in Table 7.

TABLE 7.—DORÉ FURNACE DIVERSIONS

	Silver	Gold	Route
Charged to furnace	1.0000	1.0000	
Rich slag	0.0250	0.0150	Doré furnace
Poor slag	0.0100	0.0015	Anode furnace
Flue dust	0.0100	0.0010	Doré furnace
Cobbing	0.0020	0.0012	Anode furnace
Total diversions	0.0470	0.0187	
Net output	0.9530	0.9813	

Summary of Circulating Metals.—We are now in a position to revise Table 2 by the application of the diversion factors for circulating metals in order to show what proportion of the metals entering the process emerge directly in the period given in that table. This summary of diversions is given in Table 8.

The figures of Table 8 show that but 77 per cent of the copper, 81 per cent of the silver, and 84 per cent of the gold entering the plant go directly through the process in

TABLE 8.—SUMMARY OF DIVERSIONS

	Copper		Silver		Gold	
	Factor	Cumulative	Factor	Cumulative	Factor	Cumulative
Weighing and sampling	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
Anode furnaces........	0.9918	0.9918	0.9926	0.9926	0.9961	0.9961
Tank house............	0.8008	0.7942	0.8600	0.8556	0.8600	0.8566
Refining furnaces......	0.9659	0.7671				
Furnacing slimes.......	......	......	0.9530	0.8154	0.9813	0.8406
Parting Doré..........	......	......	1.0000	0.8154	1.0000	0.8406
Melting silver.........	......	......	1.0000	0.8154	1.0000	0.8406
Refining gold..........	......	......	0.9917	0.8086	1.0000	0.8406
Melting gold..........	......	......	1.0000	0.8086	1.0000	0.8406
Net product.........	......	0.7671	......	0.8086	......	0.8406

the 24, 34, and 37 days shown by Table 2, the balance being diverted into by-products which require retreatment. The result of this is that the actual metals in process of treatment at various stages is greater than the pig receipts or cathode output by the amount of these circulating metals. It is also obvious that as these retreated metals start through the process a second time a portion is again diverted. There are several ways of evaluating this, the simplest of which is probably to work out several terms of a continued fraction, thereby ascertaining the total metals passing through each step of the process.

Balancing Metals.—In order to get the time element we must consider the "balancing metals," or stocks held at various points in the process in order to insure continuity of operation without disproportionate cost. This is done graphically in Fig. 6, where the numbers represent days. Where they occur between the rectangles representing steps in the process they stand for the average number of days output at that point held in stock; where they occur inside or alongside the rectangles they represent the days in process shown by Table 2.

We can now proceed to construct the diagrams showing the unit-days lost at each step and this has been done

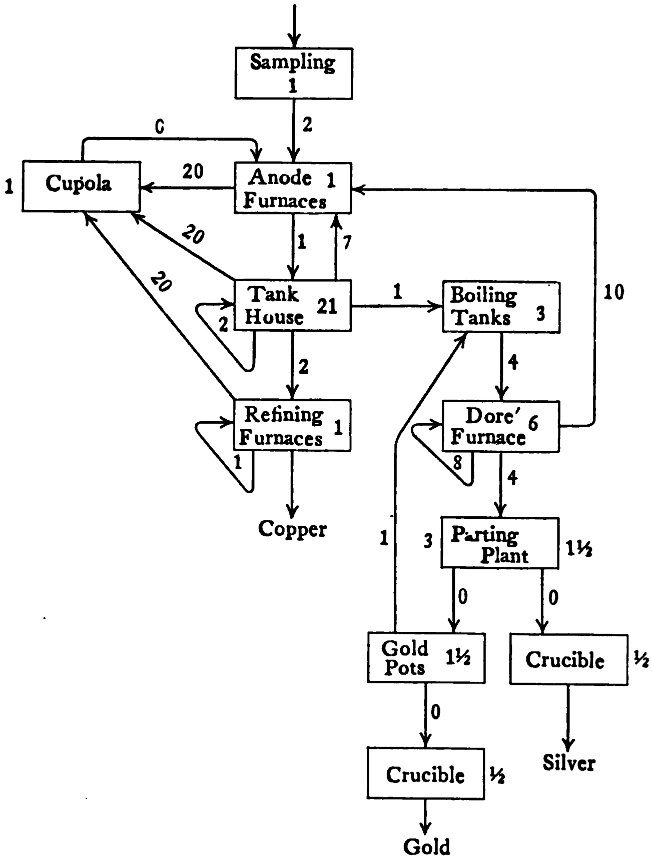
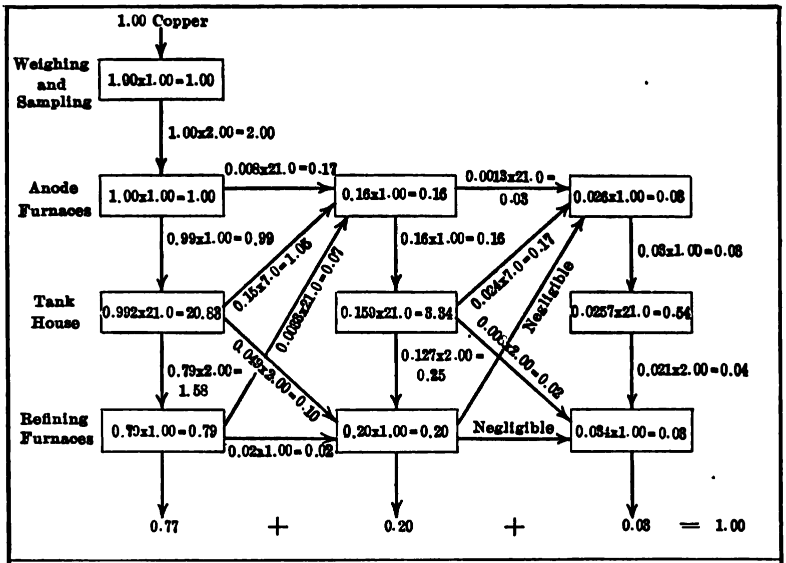

Sampling 1
2
C
1 Cupola
20
Anode 1 Furnaces
20
20
1
7
Tank House 21
2
1
Boiling Tanks 3
10
2
4
Refining Furnaces 1
1
Dore' Furnace 6
8
4
Copper
1
3
Parting Plant
1½
0
0
Gold Pots 1½
Crucible ½
0
Crucible ½
Silver
Gold

FIG. 6.—Days required for each step including balancing.

separately for the copper, silver and gold in Figs. 7, 8, and 9. Each vertical row in these figures represents one term of the continued fraction. Three terms are sufficient to approximate the total. In order to simplify the diagram the cupola has been omitted, although allowed for in the days given, and some items have been averaged in groups.

The figures are units of weight times days equals unit-days, and as one unit of weight is shown entering the process the sum of the unit-days is the actual total days that unit is in process.

Metals Withdrawn.—We have finally to consider the "metals withdrawn" by liquors, furnace bottoms, conductors, and molds. These are easily translated into unit-days by considering how long the plant would have to run in order to fill these storage vaults.


1.00 Copper
Weighing and Sampling
1.00x1.00=1.00
1.00x2.00=2.00
Anode Furnaces
1.00x1.00=1.00
0.008x21.0=0.17
0.16x1.00=0.16
0.0013x21.0=0.03
0.026x1.00=0.08
0.99x1.00=0.99
0.15x7.0=1.06
0.0033x21.0=0.07
0.16x1.00=0.16
0.024x7.0=0.17
Negligible
0.08x1.00=0.08
Tank House
0.992x21.0=20.83
0.159x21.0=3.34
0.0257x21.0=0.54
0.049x2.00=0.10
0.008x2.00=0.02
0.79x2.00=1.58
0.127x2.00=0.25
0.021x2.00=0.04
Refining Furnaces
0.79x1.00=0.79
0.02x1.00=0.02
0.20x1.00=0.20
Negligible
0.034x1.00=0.08
0.77
+
0.20
+
0.08
= 1.00

1.00	Entering Plant	24.00	Days Direct
1.18	Entering Anode Furnaces	3.93	Days Circulating
1.18	" Tank House	6.67	Days Balancing
1.02	" Refining Furnaces	34.60	Days Total

FIG. 7.—Days in process—copper.

Liquors.—We have two main bodies of liquor to consider, the copper sulphate electrolyte in the tank house and the silver nitrate electrolyte in the parting plant, the latter carrying negligible amounts of copper, however.

In the tank house in addition to the liquor actually in the tanks there is a large additional quantity in the piping system and sumps. In general in a large plant there is required about 20 lb. of liquor per pound per day of copper treated. As the electrolyte runs about 3 per cent in copper this is equivalent to saying that 0.6 days output of the plant will be required to stock up the electrolyte.

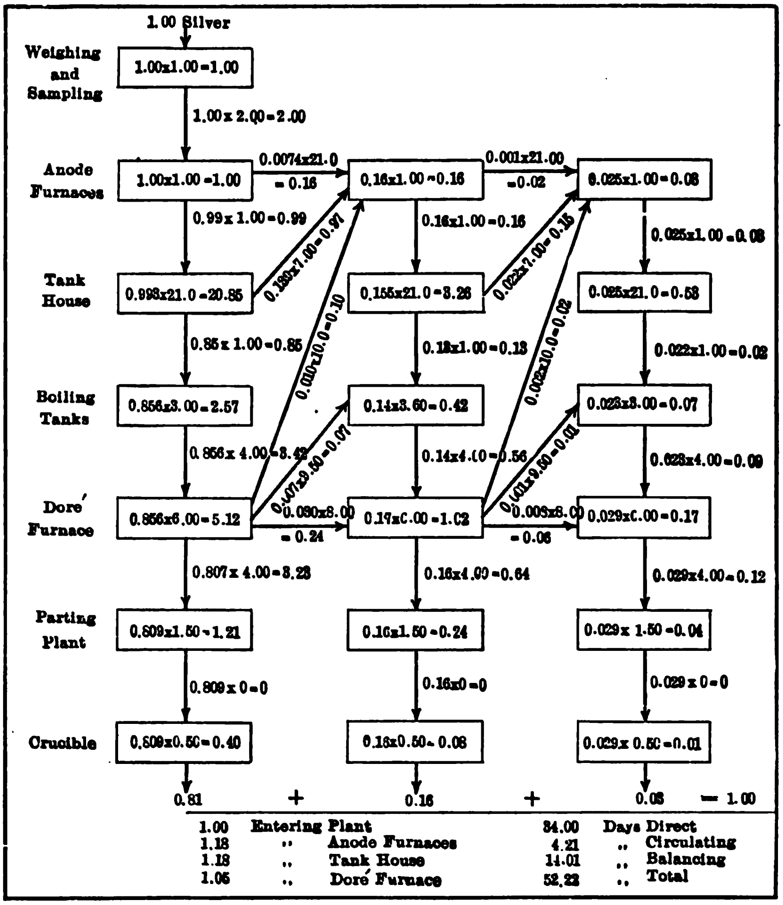
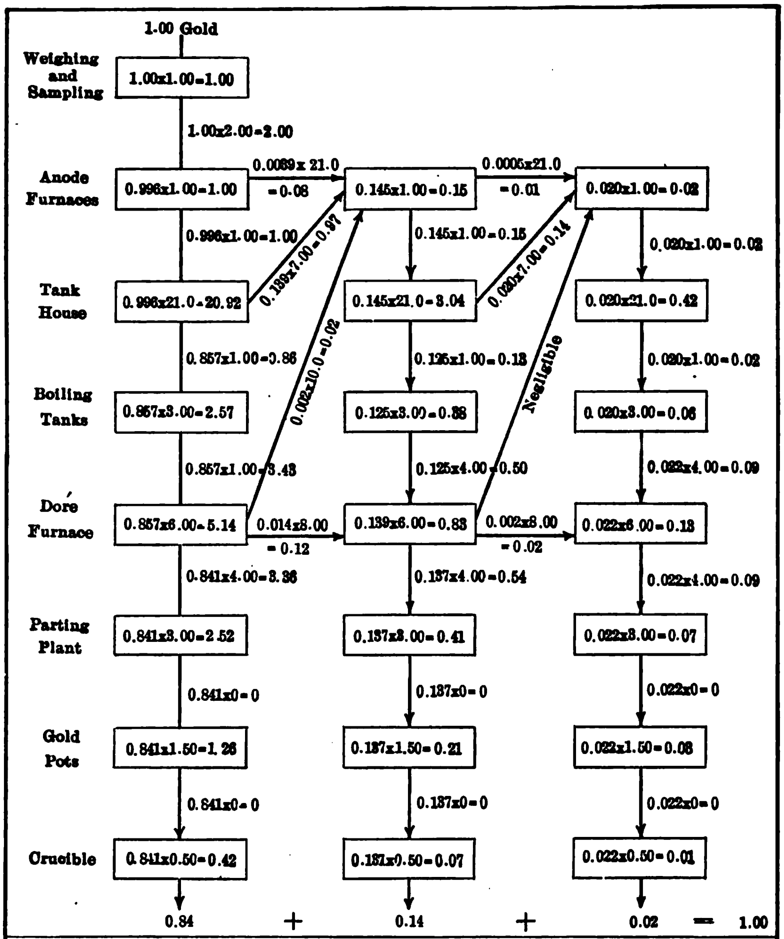

1.00 Silver
Weighing and Sampling
1.00x1.00=1.00
1.00x 2.00=2.00
Anode Furnaces
1.00x1.00=1.00
0.0074x21.0 =0.16
0.16x1.00=0.16
0.001x21.00 =0.02
0.025x1.00=0.03
0.99x 1.00=0.99
0.139x7.00=0.97
0.16x1.00=0.16
0.022x7.00=0.15
0.025x1.00=0.03
Tank House
0.993x21.0=20.85
0.155x21.0=3.26
0.025x21.0=0.53
0.85x 1.00=0.85
0.010x10.0=0.10
0.13x1.00=0.13
0.002x10.0=0.02
0.022x1.00=0.02
Boiling Tanks
0.856x3.00=2.57
0.14x3.60=0.42
0.023x3.00=0.07
0.856x 4.00=3.42
0.007x9.50=0.07
0.14x4.00=0.56
0.001x9.50=0.01
0.023x4.00=0.09
Doré Furnace
0.856x6.00=5.12
0.030x8.00 =0.24
0.17x6.00=1.02
0.008x8.00 =0.06
0.029x6.00=0.17
0.807x 4.00=3.23
0.16x4.00=0.64
0.029x4.00=0.12
Parting Plant
0.809x1.50=1.21
0.16x1.50=0.24
0.029x 1.50=0.04
0.809x 0=0
0.16x0=0
0.029x 0=0
Crucible
0.809x0.50=0.40
0.16x0.50=0.08
0.029x 0.50=0.01
0.81 + 0.16 + 0.03 = 1.00
1.00 Entering Plant
1.18 " Anode Furnaces
1.18 " Tank House
1.06 " Doré Furnace
34.00 Days Direct
4.21 " Circulating
14.01 " Balancing
52.22 " Total

FIG. 8.—Days in process—silver.

In the parting plant this factor is a little less, say 0.4 day, as there is not the circulating system to allow for.

Furnace Bottoms.—There are four main furnace bottom absorptions, anode, refining, cupola, and doré. The anode and refining furnaces are alike except that some 18 per cent more capacity is required in the anode department as shown in Fig. 7, and that the refining furnace ties up no silver and gold. An anode furnace will absorb from 100 to 400 lb. of copper per square foot of hearth area, depending upon the age, thickness and composition of the bottom.


1.00 Gold
Weighing and Sampling
1.00x1.00=1.00
1.00x2.00=2.00
Anode Furnaces
0.996x1.00=1.00
0.0039x 21.0 =0.08
0.145x1.00=0.15
0.0005x21.0 =0.01
0.020x1.00=0.02
0.996x1.00=1.00
0.139x7.00=0.97
0.145x1.00=0.15
0.020x7.00=0.14
0.020x1.00=0.02
Tank House
0.996x21.0=20.92
0.145x21.0=3.04
0.020x21.0=0.42
0.857x1.00=0.86
0.002x10.0=0.02
0.126x1.00=0.13
Negligible
0.020x1.00=0.02
Boiling Tanks
0.867x3.00=2.57
0.125x3.00=0.38
0.020x3.00=0.06
0.857x1.00=3.43
0.125x4.00=0.50
0.022x4.00=0.09
Doré Furnace
0.857x6.00=5.14
0.014x8.00 =0.12
0.139x6.00=0.83
0.002x8.00 =0.02
0.022x6.00=0.13
0.841x4.00=3.36
0.137x4.00=0.54
0.022x4.00=0.09
Parting Plant
0.841x3.00=2.52
0.137x3.00=0.41
0.022x3.00=0.07
0.841x0=0
0.137x0=0
0.022x0=0
Gold Pots
0.841x1.50=1.26
0.137x1.50=0.21
0.022x1.50=0.03
0.841x0=0
0.137x0=0
0.022x0=0
Crucible
0.841x0.50=0.42
0.131x0.50=0.07
0.022x0.50=0.01
0.84 + 0.14 + 0.02 = 1.00

1.00	Entering Plant		37.00	Days Direct
1.16	"	Anode Furnaces	3.66	" Circulating
1.16	"	Tank House	13.54	" Balancing
1.02	"	Doré Furnaces	54.20	" Total

FIG. 9.—Days in process—gold.

It is customary to start the soaking of a new bottom with material lean in silver and gold and in general the relative absorption of silver is lower than the amount to be expected from the grade of bullion treated; this ratio changes with age, however, and gold in particular seems to concentrate in the bottom.

For our purpose we may assume 0.40 days copper for the complete absorption of the furnace and flues of a refining unit. This will become 0.47 days for an anode furnace. The silver will be say 0.25 and gold 0.40. These figures must be increased about 30 per cent, however for reserve capacity.

The cupola bottom absorption is relatively negligible. This is due to the fact that it is occupied on but a day's treatment of only a circulating by-product.

On the other hand, the doré-furnace bottom constitutes a very large item, due to the facts that it is a small furnace which means disproportionate brickwork, and that it treats something more than the entire silver and gold output in six day charges. The net result is that this accounts for 12 days silver and 10 days gold.

The small absorption in the crucibles is neglected.

Conductors.—We next have the copper tied up in conductors, etc., in the tank house and the silver in contact pieces leading the current in and out of the cells in the parting plant.

These copper parts in the tank house consist of busbars, cross rods (upon which the cathodes are hung) and starting blanks (the plates upon which the starting sheets are deposited).

It is customary to buy the main busbars outright as a charge against capital expense, so these do not enter into this discussion.

The other small parts are borrowed from the copper passing through the plant as they are made of refined copper and can be melted up at any time at a day's notice, were some extraordinary market condition to call for a final accounting in refined copper. Of course this loan has to be paid for in "metal interest" as it correspondingly lengthens the time required for refining. This method is really no different from that pursued in casting lugs upon the anodes in order conveniently to suspend them in the tanks.

The items in question amount to about 1.5 days production of copper.

The silver contact pieces in the parting plant are a small item, tying up about 0.1 of a day's production.

Finally we have the copper molds used for casting the wire bars, ingots, etc., and these tie up about 2.5 days production.

The total days lost from "metals withdrawn" is shown in Table 9.

TABLE 9.—METALS WITHDRAWN

	Copper	Silver	Gold
Tank house electrolyte	0.60		
Parting plant electrolyte	....	0.40	
Anode furnace bottom	0.61	0.33	0.52
Refining furnace bottoms	0.52		
Doré furnace bottoms	....	12.00	10.00
Conductors, etc.	1.50	0.10	
Molds	2.50		
Total days	5.73	12.83	10.52

We can now summarize the results of this review and Table 10 shows a total time required of 45 days for the copper, 69 days for the silver and 68 days for the gold.

TABLE 10.—SUMMARY OF METALS TIED UP

	Copper	Silver	Gold
Commercial	5.00	4.00	3.00
Technical—Direct process	24.00	34.00	37.00
Circulating	3.93	4.21	3.66
Withdrawn	5.73	12.83	10.52
Lost			
Balancing	6.67	14.01	13.54
Total days	45.33	69.05	67.72

To these figures must be added any delays due to fires, strikes and other "unforeseen" causes, and it must further be remembered that running a plant at part capacity runs up the "metals withdrawn" and some other items.

CHAPTER III

TANK RESISTANCE

The cost of power is always a considerable and usually a major item in any metallurgical process based upon electrolysis. In the ideal refining cell the energy consumption would be zero and the quantity of metal recovered per kilowatt-hour therefore infinite, as the energy liberated at the anode would just offset that required at the cathode. In practice there are ahost of resistances and counter electromotive forces to be overcome, and a detailed study is necessary in order to understand the possibilities of improvement in any given case. In this chapter practice in copper refining by the multiple process will be inquired into as an example.

TABLE 11.—CLASSIFICATION OF TANK RESISTANCE

Item	Class	Nature
Busbar joints	Contact	Ohmic
Busbars	Conductor	Ohmic
Anode contact	Contact	Ohmic
Anode lug	Conductor	Ohmic
Anode	Conductor	Ohmic
Surface phenomena	Transfer	Ohmic
Solution of anode	Electrochemical	e.m.f.
Slimes	Resistor	Ohmic
Electrolyte	Conductor	Ohmic
Deposition of cathode	Electrochemical	e.m.f.
Surface phenomena	Transfer	Ohmic
Cathode	Conductor	Ohmic
Cathode loops	Conductor	Ohmic
Loop contacts	Contact	Ohmic
Rod	Conductor	Ohmic
Rod contact	Contact	Ohmic
Busbars	Conductor	Ohmic
Busbar joints	Contact	Ohmic

The pounds of copper recovered per kw.-hr. expended at the switchboard depends upon the current efficiency, the current density and the items, both real and apparent, which make up tank resistance. The last is the subject of our present inquiry.

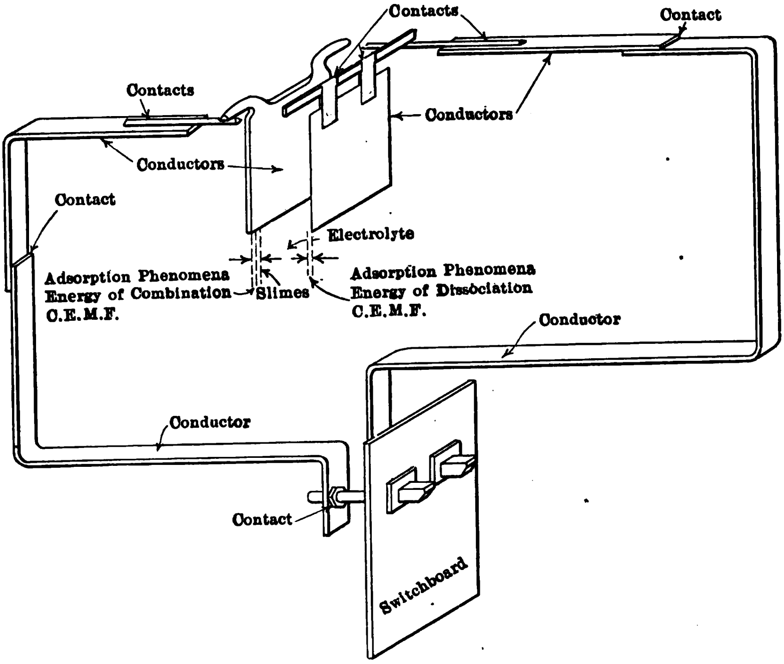

Contacts
Contact
Contacts
Conductors
Conductors
Contact
Electrolyte
Adsorption Phenomena
Energy of Combination
C.E.M.F.
Slimes
Adsorption Phenomena
Energy of Dissociation
C.E.M.F.
Conductor
Conductor
Contact
Switchboard

FIG. 10.—Diagram of circuit.

If we follow the course of the current from the positive pole at the switchboard, through the tank house and back to the negative pole, we shall find the series of obstacles to its passage shown in Table 11, taking but a single tank in circuit for an example. This is also shown diagrammatically in Fig. 10.

It is evident that in actual practice we have the items in the tank proper multiplied by the number of tanks in a circuit, or, what is the same thing, we may work out the resistance per tank, apportioning to each tank its share of the busbar resistance.

The fact that for a circuit of a single tank the busbar resistance would be inordinate, has led to putting a number of tanks in series and then to a study of the relative arrangement of groups of tanks. The placing of additional tanks in series merely distributes the voltage drop in the leads between the switchboard and the tank house.

It has been generally considered good practice to keep the line voltage down to 200 volts or less, which places an upper limit of about 600 tanks in series. Actually circuits seldom carry above 400 tanks, and this is sufficient to make the incoming leads amount to but 3 or 4 per cent of the total voltage drop.

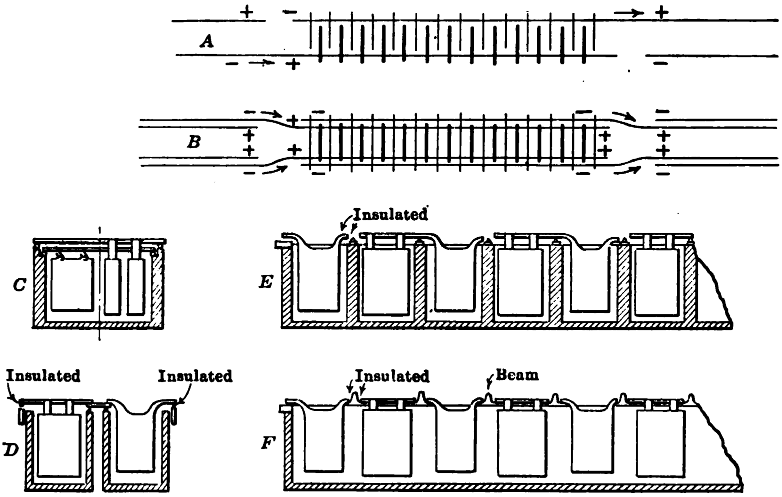


FIG. 11.—Various tank and electrode arrangements.

Figure 11 shows the evolution of tank connections. *A* is the arrangement used in the first small installations. *B* is a modification employed at the old Anaconda refinery, long since dismantled. Here the parallel conductors resulted in halving the contact resistance between conductor-bars and tanks without using any more copper, as each bar was made half-size (*C*).

Then *A* was expanded into twin tanks, as shown in *D*. This results in halving the conductor-bars required, saving copper investment as well as voltage drop. Further, as the connections between twin tanks placed individual anodes and cathodes in independent pairs, it was claimed that a short circuit between electrodes in one tank was limited in its damage to efficiency by the resistance in series in the adjoining tank.

The old Anaconda tank *C* partly met this argument in that it was very wide, and two anodes were hung side by side from a single cross-bar. This required hanging the anodes by hooks, however, and this in turn increased the number of contacts.

Then came the Walker system, shown at *E*, where the idea of *B* was expanded indefinitely, it being found feasible to sacrifice accessibility, which was still preserved on one side of each tank at *D*, to power and investment saving. This resulted in a great saving in conductor-bars, and has been generally adopted. The connecting strips shown at *B* were dropped and a small triangular bar running the length of the tank partition substituted without appreciable loss in efficiency. These bars are very small in cross-section, as they carry but half the current flowing through a single electrode when a tank is in normal condition.

Finally we have at *F* a further extension of the group idea, which has been proposed by several, in which the individual tanks are merged into one great basin, the Walker formation of electrode connections being virtually maintained, the tank partitions and triangular bars being replaced by a suitable iron beam to carry the load of the electrodes. This plan has received but a limited application, as it introduces in a modified form some of the disadvantages of the series system due to higher voltages without compensating gains. It would greatly decrease the first cost of a tank house, however, as well as that of tank repairs.

An idea of the magnitude of the different items constituting tank resistance may be obtained from Table 12, which gives the results of an analysis I made a good many years ago of a tank house built on system *D*. It must be understood that the ohmic value given for counter electromotive force is simply the apparent equivalent under the conditions of operation, and further that in order to reconcile this resistance exactly with volts divided by amperes the current efficiency corrected for chemical corrosion would have to be allowed for.

Following this introduction, and keeping in mind that it is possible to reduce any of these resistances to very low values by changes in either construction or methods of operation, we shall now discuss these possibilities item by item. We have in general (1) carrying the current to and from the electrodes, (2) from the electrodes to the electrolyte, and (3) across the electrolyte, and we shall regroup the items in Table 11 in this fashion in order to avoid repetition.

TABLE 12.—ANALYSIS OF TANK RESISTANCE

Item	Ohms per tank	Per cent of total
A. Electrolyte	0.0000444	55.1
B. Metallic conductors	0.0000131	16.2
C. Contacts	0.0000113	14.0
D. Counter electromotive force	0.0000040	5.0
E. Slimes, etc., by difference	0.0000078	9.7
Total	0.0000806	100.0
A. Electrolyte	0.0000444	55.1
B. a. Leads	0.0000024	3.0
b. Conductor bars	0.0000085	10.5
c. Anodes	0.0000002	0.25
d. Cathode rods	0.0000010	1.2
e. Cathodes	0.0000008	1.0
f. Connection strips	0.0000002	0.25
C. a. Anode contact	0.0000026	3.2
b. Cathode loop contact	0.0000043	5.3
c. Cathode rod contact	0.0000044	5.5
D. Counter electromotive force	0.0000040	5.0
E. Slimes, etc., by difference	0.0000078	9.7
Total	0.0000806	100.0

Conductors.—These consist of the leads from the switchboard to the tanks, the connections between the leads and the electrodes and the electrodes themselves. As the resistance of a conductor varies directly as its length and inversely as its cross-section, while its first cost varies as the product of the two, we have from both points of view to make each connection as short as possible, while the cross-section involves a balance between first cost, the

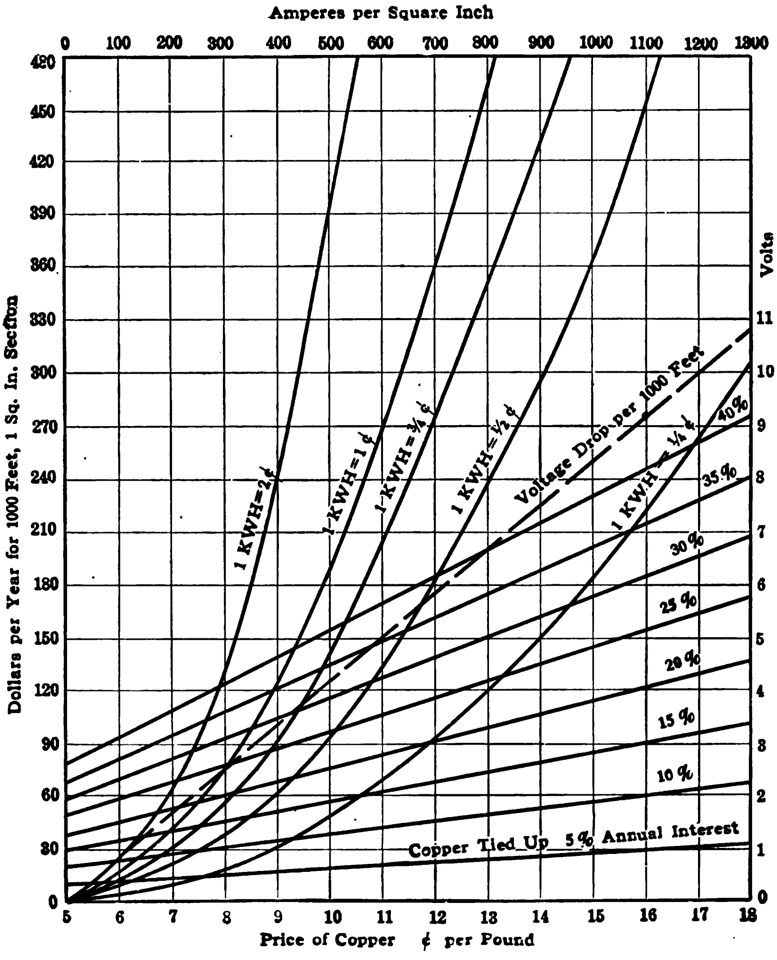


FIG. 12.—Data for determining most economical section of copper conductors.

cost of power and sometimes strength. Carrying capacity does not enter as far as heating goes, as the other factors place this far on the safe side.

As we have a steady full load twenty-four hours a day, we can apply directly Thomson's law that the cheapest cross-section will be that for which the interest on the copper investment just equals the cost of the power lost by the voltage drop. The corresponding current density to be chosen for the conductors will vary greatly with the cost data for the individual case. This density is usually in the neighborhood of 500 amp. per sq. in., as against 1000 amp. commonly used in switchboard work.

Figure 12 shows these relations graphically. A standard conductor 1000 ft. long and 1 sq. in. in cross-section, is taken, and two sets of curves superimposed, the first being the interest charges on the copper in dollars per year for different prices per pound for copper and various rates of interest, and the second being the power loss in dollars per year for different currents and various costs per kw. hr.

It is in this way possible to select the basic data and at once equate the two values.

For example, suppose we take copper at 15 cents a pound, interest at 10 per cent, and a kw.-hr. at ½ cent, we enter the diagram at the bottom of the 15-cent line, and note that it intersects the 10 per cent line at $57 a year as our interest charge. This same $57 a year line, however, intersects the curve for ½ cent kw.-hr. at an abscissa corresponding to 390 amp. and as the conductor has 1 sq. in. area, this means a current density of 390 amp. per sq. in. An additional line on the diagram tells us that the voltage drop will be 3.4 volts per 1000 ft. of conductor. If we have 300 tanks on a circuit absorbing 0.32 volt each, and the generator is 500 ft. away, we should have a line voltage of 100 volts and 3.4 per cent loss in the leads, exclusive of any excess drop at joints in the bars.

The same principle applies to the various connections around the tanks, always remembering to figure out just what current each individual piece is carrying. Here, however, the element of strength enters in, and it may be necessary to make a cathode rod, for example, larger than is required for current carrying capacity, in order to obtain requisite stiffness. In some plants copper-covered iron is employed in such cases.

In the case of the electrodes themselves, the body of the cathode and anode are of ample cross-section. The cathode loops, however, are sometimes overlooked. Suppose we have a cathode 3 feet square, operating at a current density (of electrolysis) of 20 amp. per sq. ft., hung by two loops, each 3 in. wide, cut from starting sheets 0.02 in. thick. We shall have a current of 3 × 3 × 2 × 20, or 360 amp. carried by a conductor 4 × 3 × 0.02, or 0.24 sq. in. in section, giving a density of 1500 amp. per sq. in., or far above the economical range.

The anode metal will be of low conductivity, but the lug through which the current enters is usually of ample size.

Contacts.—It has been shown that the size of the metallic conductors is specifically determined by the cost of power and other considerations. In the case of contact resistances we have no desirable value, the proper course being to make them just as small as possible. Experiments show a contact resistance to be truly ohmic in character, the voltage across a given contact increasing directly as the current is increased. It appears to be due primarily to adsorbed air on the surfaces in contact, and secondarily to oxide or other foreign matter. Pressure and moisture lower the resistance.

We have two classes of contacts, one where permanent joints can be mechanically made, and the other where temporary gravity joints must be used. It is customary on sliding joints, as in the case of switch surfaces, to keep the surface current density down to about 50 amp. per sq. in. In the case of busbars this figure can be greatly exceeded. A planed joint firmly bolted together will operate at 200 amp. per sq. in. without showing appreciable voltage drop—that is, 1 millivolt.

In the case of the loose gravity joints between the electrodes and their supports, we have one of the large sources of waste power in the system which can be attacked along three lines, namely, decreasing the number of contacts, increasing the acting pressure and improving the condition of the surfaces.

As the surest way of cutting down the resistance at a joint is to eliminate the joint, study has naturally been directed toward securing the minimum number of loose joints in series compatible with efficient handling of the electrodes. The various forms of anode and cathode suspension are shown in Fig. 13.

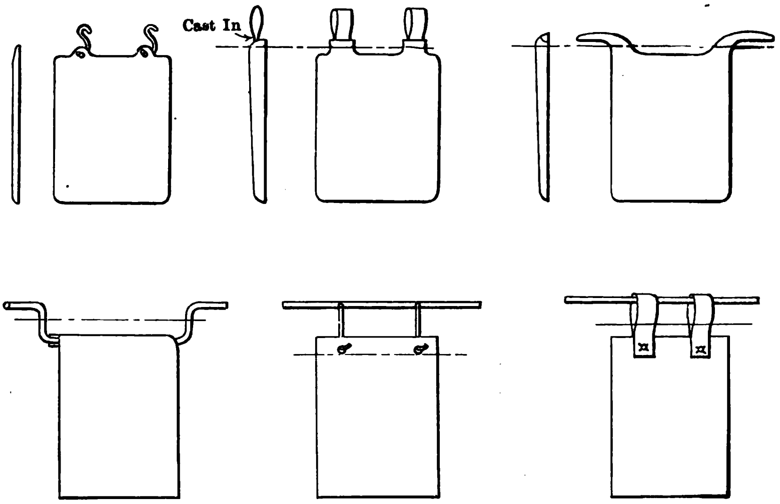


FIG. 13.—Various forms of electrodes.

The anodes suspended by hooks have one single and two twin contacts equivalent to two series contacts; those with loops, one single and one twin, equivalent to one and a half; while the standard anode, with cast lugs, has but the single contact at the conductor or triangular bar.

The cathodes have gone through the evolution shown. The first example gives but a single contact, but has been abandoned on account of trouble with corrosion of the rods in spite of painting at the solution line. The others give one and a half contacts, but a more reliable method of suspension. The part of the loop beneath the surface of the liquor does not matter, as this joint is soon covered by the deposited copper.

At one of the refineries work has been done on eliminating another contact by doing away with the triangular bars, allowing the cathode rod to rest directly on the lug of an anode in the adjoining tank. This is in effect returning to the connection shown at *D* in Fig. 11, but eliminating the connection strip.

The minimum number of loose contacts we can get along with is, therefore, one-half entering the anode, one-half at the cathode loops, and one-half leaving the cathode rod, or an equivalent of one and a half, while the usual practice is one anode and one and a half cathode, electrodes being alive at one lug only.

The pressure exerted upon the two surfaces has a great deal to do with the resistance shown to the passage of the current. For example, the contact resistance between the triangular bar and the anode increases day by day as the anode dissolves away, and one of the loop contacts will show almost as high a resistance as the cathode bar contact, which has twice the current but twice the weight.

Various devices have, therefore, been tried to increase this pressure, notably plugs and clamps. At one plant holes were drilled in the anode lugs and these were reamed out to receive a tapered copper plug connected permanently by a short cable to the busbar. This is of no advantage if the original contact is kept clean, because we are dealing with such a low order of resistances that the short cable will have too high a resistance to be of much service as a parallel circuit. Of course, it does prevent excessive values for the joint, but with present-day methods of tank inspection these are not allowed to occur.

A number of years ago the writer tried out thoroughly the use of spring clips on the cathode loops and rod connections. These gave very encouraging results, cutting out over 80 per cent of the resistance. When the cost of renewing the clips from time to time, the labor of handling them and the additional hindrance in working around the tank was allowed for, some of this margin was eaten up. The great offset to such a plan, however, has been the improvement in keeping contacts clean, taken up below.

Much has been done in the lowering of contact resistance by shaping one of the members as a wedge which will bring a heavy unit pressure upon the other. This is the idea in the triangular bar, and it has been carried further in the proposal to have a wedge of a different angle from a corresponding groove which would result in crowding.

Finally we have the very important matter of the condition of the two surfaces. Contact resistances develop considerable heat, and this means that any drippings of electrolyte in the neighborhood of a contact will soon be converted into anhydrous copper sulphate forming a coating which effectually prevents the existence of a perfect contact.

The first principle is, therefore, to keep the contacts clean, and when set up the rods and under surface of the anode lugs are always brightened with sandpaper or its equivalent.

Various means have been tried for making a better union physically. Mercury cups are not practical for many reasons, but amalgamating the surfaces is possible. This gives excellent results, but the cost of the amalgam used, plus that of the labor applying it, amounts to more than the saving.

At one time a scheme was advanced for keeping the anode and cathode rod contacts wet by substituting shallow copper gutters for the triangular bars and allowing water to flow therein. This also gave good results but at too great an expense for proper maintenance. Finally it was found that oiling a contact after shining it did not interfere with the contact itself, while it did serve to keep it clean for a long time, and cost almost nothing to apply.

The result of these various developments has been to cut in half the values for contact resistance given in Table 12.

It must not be thought that because the ohmic values are very small the financial equivalents are likewise so. Take the saving of one-half of 0.0000113 ohms per tank just spoken of, and assume power at ½ cent per kw.-hr., 10,000 amp. on a circuit and 1500 tanks in the tank house. The saving will be $\frac{0.0000113}{2} \times \frac{10{,}000 \times 10{,}000}{1000} \times 1500$ or 848 kw., equivalent to 848 × 24 × 0.005 or $102 a day.

Transfer Resistance.—We come now to the transfer of the current between the electrodes and the electrolyte. This is a field which is very difficult properly to resolve into the several component factors. In true refining the total value is not very great, but bad conditions, such as poor circulation of the electrolyte, foul anodes, etc., may greatly increase the normal value. In general, we have to deal with counter electro-motive force, the ohmic resistance of an adsorbed gas film and the screening effect of the slimes.

The counter electro-motive force is the opposing voltage due to the cell acting as a battery, and is due to the difference in composition between the anode and the cathode, and to the differences in concentration of the electrolyte around the two electrodes.

The first cause is small in its effect except in the insoluble anode tanks used for controlling the copper contents of the electrolyte which operate at about six times the voltage required for refining cells.

The second is due to the fact that the circulation of the electrolyte, which must be gentle in order to avoid stirring up the anode slimes and thereby contaminating the cathodes, is not sufficient to sweep away from the face of the anode the descending layer of solution rich in copper sulphate formed by the electrolysis, nor the corresponding lean layer which rises at the surface of the cathode.

This forms a Cu—$CuSO_4$—Cu concentration cell with a small electromotive force tending to equalize the differences in concentration and therefore against the applied voltage.

It is quite easy to measure these two effects jointly by taking careful current-voltage readings while varying the current over a range not great enough seriously to change the conditions. If these readings are plotted and a straight line drawn through the points, this line will intersect the voltage base line at the value of the counter electro-motive force on the circuit. In practice this amounts to from 0.01 to 0.02 volt per tank.

The ohmic resistance of what is doubtless an adsorbed gas film on each electrode is considerable and under some conditions may become enormous.

If we explore the potential gradient between anode and cathode we shall find a sudden drop as we leave the anode, a gradual slope across the electrolyte and another sudden drop as we reach the cathode. This film acts as a true ohmic resistance and has a temperature coefficient.

The various addition agents which have proved of such assistance in obtaining smooth deposits act markedly on this resistance. A moderate dose of gelatin in the electrolyte will increase the overall voltage required as much as 40 per cent.

Then we have the screening effect of a curtain of poorly conducting slimes on the face of the anode. A well-refined high-grade anode makes a loose granular slime which offers but little resistance to the passage of the current; less favorable conditions result in a thick greasy slime that is pierced in places by the current making for high resistance and irregular solution of the anode. The latter condition often results in what are sometimes called "crazy tanks" where a voltmeter across the tank will give no constant reading but jumps violently back and forth between a normal tank voltage and one about three times as great.

The value of the resistance due to adsorbed gas and slimes can only be obtained by difference between the sum of the values found for all other items and the total overall voltage. This is generally about 10 per cent of the total resistance in circuit. It probably lies chiefly in the gas film and further study may discover some way of reducing this factor.

Electrolyte.—We come finally to the resistance of the electrolyte itself and this brings up three questions, the necessary distance between the anode and the cathode, the composition of the electrolyte and its temperature. As the electrolyte comprises over half the total resistance in circuit, it is necessary that it be considered in detail.

The question of permissible electrode spacing belongs under the heading of current efficiency which we are not here discussing. It also depends upon the advisable age of electrodes, or particularly upon how many crops of cathodes correspond to a single set of anodes as each crop will operate on a wider spacing than the previous one. When three or more crops are drawn it may pay to respace the tank.

Spacing also is related indirectly to current density as additional density greatly increases the difficulty of working at close spacing. The foulness of the anode also has a bearing as voluminous or flocculent slimes demand greater distance in the interest of a clean cathode.

The average thickness of liquid column has been gradusally reduced from 2 in. to about an inch and a quarter, due largely to better control of the physical character of deposits in late years. During the same period current densities have increased and the area of electrodes has been enlarged so that the full value of the improvement in deposit has been apportioned in several directions.

The composition of the electrolyte is very important. It may be considered to be made up of sulphuric acid, cupric sulphate, impurities in the form of sulphates or more complex compounds such as arseniates, etc., and finally addition agents.

The conductivity depends chiefly upon the mobile hydrogen ions from the dissociation of the sulphuric acid and, as would be expected, increasing the free acid within certain limits markedly lowers the resistance of the electrolyte.

There are limitations imposed by two difficulties. As we have a solution of mixed sulphates we are bound by the habits of isohydric solutions, the amount of dissociated hydrogen depending upon the relative concentration of the other sulphates as well as upon that of the sulphuric acid.

The other limit is due to the fact that too great a hydrogen concentration affects unfavorably the electrode surface phenomena discussed under a previous heading. The net result of these two limitations is that very high percentages of free acid do not give improved over-all results and it is not customary to carry above 13 per cent.

These same arguments require carrying as small an amount of copper sulphate in solution as shall give a satisfactory deposit at the cathode. This is borne out in practice although the variation in conductivity is not very great with changes in the copper concentration. A complete set of measurements of the conductivity of different mixtures of copper sulphate and sulphuric acid has been made by Richardson and Taylor.[1]

With good operating conditions the copper in the electrolyte can be carried down below 2 per cent without impairing the cathode deposit; were it possible to increase the circulation, even lower values could be considered. It is unwise to proceed too far in this direction, however, and values between 2.5 and 3.0 per cent are considered good practice. Even under difficult operating conditions there is no particular advantage in carrying over 3 per cent copper. The early electrolytes were carried at 4 per cent copper and 8 per cent free acid; these have gradually been modified to 2.75 per cent copper and 12 per cent free acid.

The specific resistance of such an electrolyte at 120°F. will be about 0.7 ohm per cubic inch. The various impurities in the electrolyte will increase this anywhere from 5 to 15 per cent so that a working value will be about 0.8 ohm. A reasonably accurate measurement of this resistance may be obtained with an ordinary voltmeter and two copper electrodes if the column of electrolyte measured be long enough to render negligible the voltage effects at the electrodes. Whether this length has been obtained may be tested by increasing it and seeing if any lower readings per unit of length are obtained. Eighteen inches between electrodes will generally be found sufficient.

The minute quantities of organic addition agents have probably but slight effect upon the conductivity of the electrolyte, their effect upon the resistance being at the electrodes. On the other hand, inorganic agents such as ammonium sulphate, used to be added in large quantities and these had, of course, to be reckoned with, any increase in sulphates tending to drive back the dissociation of hydrogen ions.

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[1] *Trans.* Am. Electroch. Soc., Vol. xx, p. 179.

The temperature of the electrolyte is a very important matter. In the first place the electrolyte itself has a positive temperature coefficient of about 0.5 per cent per °F. There is not only this enormous premium set upon running with the solution hot, but in addition the electrode conditions are greatly benefited. The disadvantages are the cost of heating, the increased humidity of the atmosphere in the tank house and the increased growth of copper in the electrolyte by chemical action.

It is customary to heat the liquors to about 135°F. in the circulation wells and this temperature drops 10 to 20 deg. in passing through the system, resulting in different resistances in different tanks.

Some of the older plants had long cascades of tanks, the electrolyte flowing through five or six tanks in series; modern plants have generally but two tanks in series so that the temperature inequalities are not so severe as formerly.

We have now discussed item by item the various components of tank resistance. In making these up into a sum to compare with the readings of the switchboard instruments we must see to it that we have properly allowed for the number of series-parallel circuits formed by the multitude of anode-cathode pairs, for the proportion of tanks which are "locked out" so many hours a day for replacement of electrodes and cleaning of slimes, for the special conditions in insoluble anode tanks and finally for the negative factor introduced by imperfect current efficiency which provides a by-pass or parallel circuit for a certain part of the current, the discussion of which will be taken up in a later chapter.

CHAPTER IV

CURRENT DENSITY

The current density, or amperes per square foot of active cathode surface, is the factor in an electrolytic process, such as copper refining, upon which above all others the design and operation of the plant depend, as upon it hangs a string of minor factors which must be properly correlated in order to obtain the best return upon the investment. These factors may be classified under cost per pound of cathodes recovered, first cost of plant, and metallurgical purity of product.

Aside from commercial considerations there is a limit to the density which can be employed imposed by the temperature of the electrolyte. By far the larger part of the electrical energy called for is converted into heat in overcoming the ohmic resistance of the cells and the temperature of the electrolyte rises until the heat losses offset the C^2R gain.

The electrodes are spaced so closely in the tanks that the equivalent energy to be dissipated is quite large and further at about 150°F. a liquid will begin to steam sufficiently to make a tank room too foggy for comfort or for efficient inspection. As a starting point we may first examine this question of temperature of electrolyte.

Temperature of Electrolyte.—In ordinary practice with moderate densities the electrical energy is supplemented by a certain amount of either live or exhaust steam to obtain the desired temperature of operation generally in the neighborhood of 130°F. This requires a balancing of the cost of heating against the gains resulting. In the last chapter we have considered in detail the question of tank resistance and took as an example a certain case which gave the distribution of resistance shown in Table 12.

Increasing the temperature of the electrolyte will lower its resistance by an amount proportionate to the increase and to its temperature coefficient of about 0.5 per cent per °F. It will increase the resistance of the various metallic resistances and contacts which it can affect.

As the anodes and cathodes are the only submerged metallic resistances and as they are of negligible resistance, we may turn to the exposed resistances and contacts. The leads and conductor bars along the sides of the tanks are too far removed from the source of heat to be much affected. The contacts are kept well above room temperature by their own C^2R loss.

The temperature coefficient of copper is plus 0.24 per cent per °F.

I think we may safely assume that the total change in these minor resistances with change in temperature of the electrolyte is very small. The "transfer" resistance at the surfaces of the electrodes is markedly lowered by increase of temperature, but this gain is large only in the lower part of the temperature range.

We may therefore consider the temperature coefficient as approximately minus 0.5 per cent per °F. at high temperatures and a larger figure at low temperatures due to the added change in "transfer" resistance.

When running at about sixteen amperes per square foot of cathode surface without the use of any steam for heating, the electrolyte in an average system will run about 25°F. above the temperature of the atmosphere in the tank room, which latter is generally around 70°F. and very humid unless an adequate system of forced ventilation is employed.

Some simple tests where a circuit was allowed to run without any heating steam until at temperature equilibrium and then heating as rapidly as possible in the solution wells showed the results given in Table 13.

TABLE 13.—EFFECTS OF TEMPERATURE OF ELECTROLYTE ON TANK RESISTANCE

Test No.	Ohms per tank			Deg. Fahr.			Ohms per degree	Temp. coeff. per cent
	Initial	Final	Diff.	Initial	Final	Diff.		
1	0.000094	0.000089	0.000005	102	121	19	0.00000026	0.29
2	0.000097	0.000087	0.000010	103	122	19	0.00000053	0.61
3	0.000091	0.000082	0.000009	108	128	20	0.00000045	0.55
4	0.000096	0.000088	0.000008	105.	118	13	0.00000062	0.70
Av.	0.000095	0.000087	0.000008	105	122	17	0.00000047	0.54
Current = 4400 amperes	Watts per tank without steam = 1840							

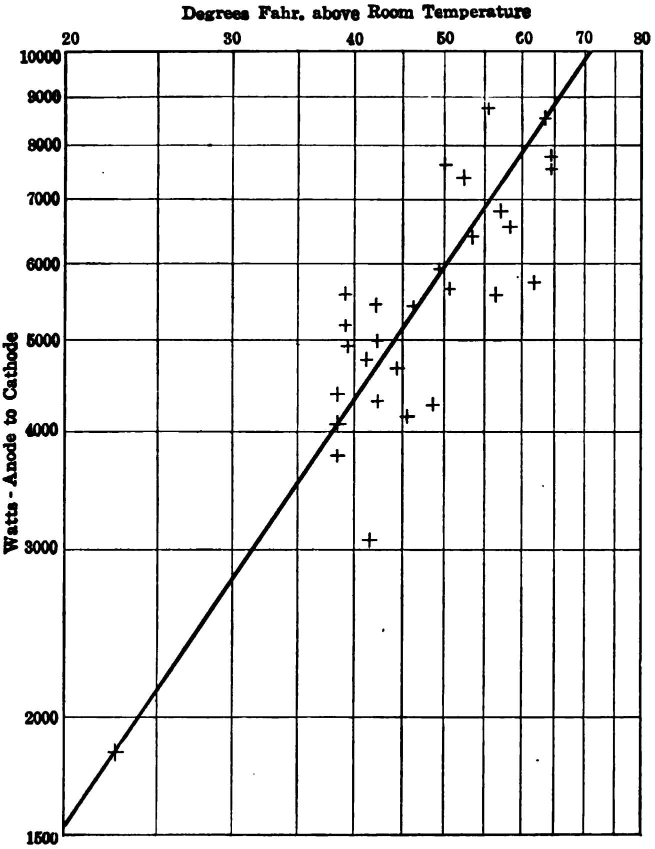

FIG. 14.—Watts to maintain temperature of electrolyte.

This temperature coefficient of 0.54 per cent per degree Fahrenheit is so large that it at once becomes apparent that the application of direct heat to the electrolyte should be considered. Some interesting tests were carried out at another plant by measuring the temperature of the electrolyte, amperes and voltage from anode ear to cathode loop, for different current densities without direct heat.

Some of the results obtained are shown in Fig. 14. The watts per tank required to maintain a certain temperature is a measure of the rate of cooling at that temperature and the curve is therefore exponential. Plotting the data on logarithmic section paper indicates a law of

$$\text{Watts per tank} = 20.8 \times (^\circ\text{F. liquor} - {}^\circ\text{F. atmosphere})^{1.45}.$$

This formula is, of course, only good for the conditions at the particular tank house where the tests were conducted. At a room temperature of 70°F. this formula would give our practical limit temperature of 150°F. in the electrolyte with 12,000 watts per tank.

Under the conditions of this set of tests the internal tank resistance would be about 0.00003 ohm and 12,000 watts would correspond to a current of 20,000 amp. and a current density of 64 amp. per square foot. This is far above any density ever likely to be applied in practice unless marked changes in the general arrangement of the process develop.

With a density of 45 amp. per square foot the electrolyte would probably run about 120°F. and the use of steam for heating would hardly be justified. At lower densities we have the usual case of heating in the solution wells by steam.

We shall see in Chapter XI that if we figure out a heat balance between live steam for heating and the saving at the boilers for decreased electrical power for electrolysis, the total cost increases as the electrolyte is heated.

The earlier plants did use live steam for heating but the more recent installations have used exhaust steam, in some cases obtained by operating some of the main generating units under partial vacuum, and this changes the entire situation.

Another result of heating the electrolyte is to increase the growth of copper in solution due to the oxidizing effect of the liquor. Copper is not ordinarily considered soluble in dilute sulphuric acid but when the solution is aerated by passing from tank to tank the oxygen dissolved brings about slow solution.

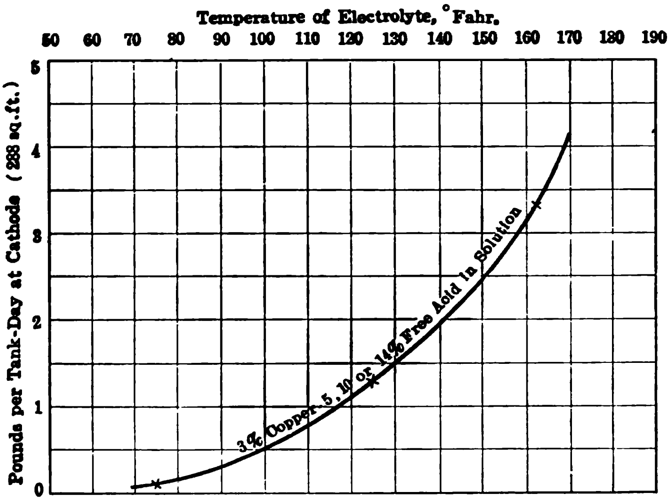

FIG. 15.—Chemical corrosion of copper by electrolyte.

Figure 15 shows the rate of action of a solution carrying 3 per cent. copper and varying percentages of free acid upon a piece of cathode copper about 3 × 3 inches, as the temperature is raised in a beaker. This shows that the degree of attack rapidly increases with rising temperature, and is practically independent of the degree of acidity. This action may or may not be desirable according to circumstances.

Where quite pure anodes are being refined the excess copper builds up in the electrolyte and is usually removed by means of insoluble anode or "liberating" tanks. As these operate at from 2.0 to 2.3 volts or some seven times as much as ordinary depositing tanks require, this power tends to offset the resistance saving due to hot electrolyte.

When, on the other hand, the anodes carry considerable percentages of nickel, cobalt, etc., a proportion of the current is employed dissolving these substances electrochemically at the anode while depositing an equivalent quantity of copper at the cathode, so that the nickel, etc., will grow in the electrolyte which is at the same time depleted in copper. Then the addition of copper by chemical corrosion is very welcome; in fact in extreme cases this effect has to be artificially increased by the use of towers of shot copper or similar means.

In general it is found necessary to use from 2 per cent. of liberating tanks at one extreme to no liberating tanks and shot towers at the other.

The temperature of the electrolyte also has a bearing upon the shrinkage in volume in the electrolyte due to evaporation. Now that it is customary to use a purifying process on a closed cycle evaporation gives almost the only means of making room for water used in rinsing the anodes and cathodes.

The final and really controlling reason for the use of warm electrolyte is the greatly improved metallurgical conditions resulting therefrom. Not only is the cathode smoother and denser, but the conditions at the dissolving surface of the anode are greatly benefited.

The increased temperature brings about a local circulation which assists in removing the dense solution of copper sulphate from the face of the anode and in preventing stratification in the tank.

When current is passed through a cold cell without any circulation of the electrolyte conditions soon become so unbalanced that the electrodes will gas, the voltage show violent fluctuations and the anode slimes be stirred up and carried in suspension, thereby fouling the cathode.

When the electrolyte is systematically circulated these bad effects are counteracted, but the rate of circulation which can be employed is limited by the eventual stirring up of the slimes mechanically.

There is in turn a current density for this limiting circulation which begins to bring about a return of the undesirable gassing and for a cold liquor and an impure anode this density is so low as to require an abnormally large plant investment.

When the electrolyte is heated this density limit is greatly raised and it was practice even in the very early days to heat the electrolyte somewhat—perhaps to 110°F.—and later this temperature has been gradually increased until 135°F. or even higher entering the tanks is not uncommon.

In series system plants the tanks have commonly been lined with some asphalt composition which softens with heat and this has made it impracticable to use temperatures as high as would be otherwise desirable, and is one of the reasons that series processes require relatively pure anodes.

In general, therefore, (1) the temperature of the electrolyte should be carried well up toward the practical limit of 150°F. in order to be able to employ as high a current density as may be desirable from the point of view of cost of operation; (2) unless a very high density permitted by very unusual conditions is employed, heating in the solution well will be required to maintain this temperature; (3) with proper exhaust steam design this heating will be financially profitable.

Power.—Assume a tank resistance of 0.0000766 ohm, a counter e.m.f. of 0.010 volt per tank, 24 pairs of 2 ft. × 3 ft. anodes and cathodes, making 288 sq. ft. of surface and 90 per cent current efficiency. As we increase the current density we shall have the conditions shown in Table 14.

This table shows that the power cost per pound of copper rises nearly in proportion to the current density employed.

It is true that we have assumed a constant tank resistance due to maintaining the electrolyte at a constant temperature by means of steam.

As the current density is raised the electrical heat dissipated in the tanks will increase, as previously discussed and this will mean that less heating steam will be

TABLE 14.—RELATION BETWEEN CURRENT DENSITY AND POWER COST

Amperes per sq. ft.	Amperes	Volts	Watts	Lbs. copper per 24 hours	Watt-hours per 24 hours	Watt-hours per lb. copper
5	1,440	0.120	173	81	4,200	52
10	2,880	0.231	665	162	16,000	99
15	4,320	0.341	1,470	243	35,300	145
20	5,760	0.451	2,600	324	62,400	193
25	7,200	0.562	4,050	405	97,200	240
30	8,640	0.672	5,810	486	139,400	287
35	10,080	0.782	7,870	567	189,000	334
40	11,520	0.892	10,280	648	246,200	381

required and this saving will give some credit to be applied against the power cost.

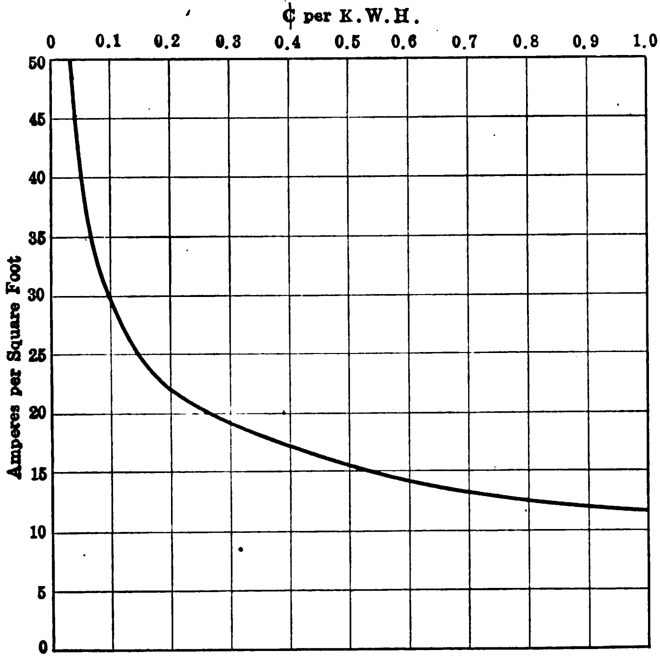

FIG. 16.—Current density *vs.* power cost in practice.

It is evident that the cost of producing a kilowatt-hour will have a great deal to do with the question; in fact it is possible to plot the power cost at various plants against the current density used and obtain quite a smooth curve. Figure 16 shows this general relation, but individual cases may show exceptions for special reasons.

First Cost of Plant.—Assume that the tank house equipment in the example taken amounts to an investment of $300 a tank and that the power plant costs $80 a kilowatt. As the former will vary with the output of cathodes per tank day and the latter with the kilowatt demand, both of which depend upon the current density, we can take the relation determined in Table 14 and ascertain the joint influence of these two factors, which has been done in Table 15.

TABLE 15.—RELATION BETWEEN CURRENT DENSITY AND COST OF PLANT

Current density	Lbs. copper per tank day	Tank investment per lb. copper per day	Watt-hours per lb copper	Watt-days per lb. copper	Power plant investment per lb. copper per day	Total Investment per lb. copper per day
5	81	$3.70	52	2.16	$0.17	$3.87
10	162	1.85	99	4.12	0.33	2.18
15	243	1.23	145	6.04	0.48	1.71
20	324	0.92	193	8.06	0.65	1.57
25	405	0.74	240	10.00	0.80	1.54
30	486	0.62	287	11.90	0.95	1.57
35	567	0.53	334	13.90	1.11	1.64
40	648	0.46	381	15.80	1.26	1.72

Labor Cost.—The main labor items in operating a tank house are for inspection work to maintain current efficiency and for inserting and drawing the electrodes as the copper moves through the process.

The higher the current density the more difficult is it to maintain the efficiency on account of the increased number of short circuits caused by rough deposits on the cathodes.

After the circulation of the electrolyte has been raised to the highest rate which will not stir up slimes and addition agents have been added to control the character of the deposit as much as possible, the only ways to improve efficiency are either steadily to increase the inspection labor or to decrease the life of the cathodes.

Actually as the density rises the efficiency in practice is sacrificed a little, the labor is increased and the age of the cathodes decreased until a balance is struck.

The cost of making starting sheets in the multiple process also enters if the weight of the individual cathodes is changed. We shall confine ourselves to an inquiry into the effect of age of electrodes upon the labor cost.

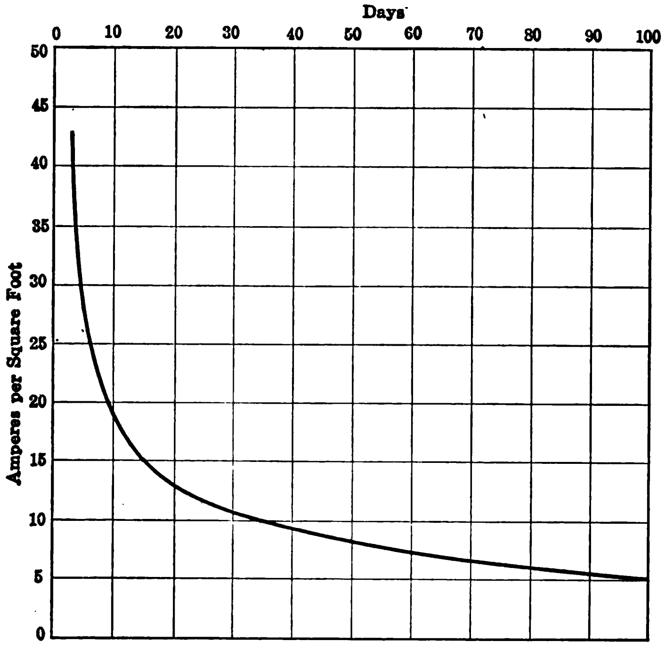

Fig. 17.—Current density *vs.* age of cathodes in practice.

Age of Electrodes.—The age of the anodes and the proportion of anode scrap made have but little connection with the current density, except that foul anodes which give heavy scrap will work at increasing disadvantage as the density is increased.

In the case of cathodes we may observe a general relation between age and density as shown by the practice at different plants and given in Fig. 17. The increasing knowledge of the value of addition agents in recent years has tended to lessen the slope of this curve, however, and the day of the very low density plant has apparently passed, in America, at least.

Taking this curve as a basis and assuming that a starting sheet costs one cent to make and that it costs two cents a cathode to handle sheets in and cathodes out of the tanks, making a total of three cents, we can figure as in Table 16 the cost of changing age with density.

TABLE 16.—RELATION BETWEEN CURRENT DENSITY AND AGE OF CATHODES

Current density	Lb. per tank day	Lb. per cathode day	Cathode age in days	Lb. per cathode	Cathodes per ton	Total per ton
5	81	3.4	100.0	340	5.9	$0.18
10	162	6.7	37.0	248	8.1	0.24
15	243	10.1	15.2	154	13.0	0.39
20	324	13.5	9.6	130	15.3	0.46
25	405	16.9	6.8	115	17.4	0.57
30	486	20.2	5.2	105	19.0	0.52
35	567	23.6	4.0	95	21.1	0.63
40	648	27.0	3.2	86	23.3	0.70

Metallurgical Effects of Current Density.—A high current density will always give trouble at the anode when treating foul material and usually bring about abnormally high voltage conditions. But even where normally pure anodes are refined the disturbance of the slimes is greater as the density is raised, due partly to the necessarily somewhat increased mechanical circulation and partly to local gassing or heat disturbances at the face of the anode.

This relation can be clearly traced in the purity of the cathode and while it is ordinarily not sufficient in magnitude to affect the commercial purity of the copper as such, it can be clearly felt in the silver and gold losses carried away in the cathodes.

The percentage of the silver and gold in the anodes which is found in the cathodes at various plants is plotted against the current density in use in Fig. 18. Where the anodes are rich in values this factor may be of some importance.

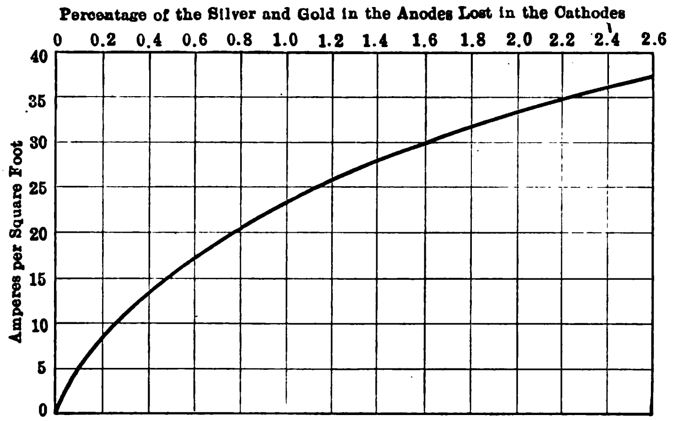

FIG. 18.—Current density *vs.* metal losses in practice.

Financing Metals in Process.—In Chapter II it was shown that the copper, silver and gold are tied up in the tank house an equivalent of 25 days in ordinary eastern practice, which means a current density of about 20 amperes per square foot. It is evident that this time will vary with any change in the density, and for simplicity's sake we shall assume that this variation will be in straight inverse proportion, although it is quite possible to change the weight of the anode or percentage of scrap at the same time.

Taking copper at a price of fifteen cents a pound and silver and gold values of varying amounts and interest at 6 per cent per annum, we have the situation shown in Table 17.

TABLE 17.—RELATION BETWEEN CURRENT DENSITY AND METALS TIED-UP

Current density	Days in tank house	Interest charges per ton at 6 per cent with silver and gold per ton at					
		$25	$50	$75	$100	$200	$300
5	100.0	$5.42	$5.83	$6.25	$6.67	$8.33	$10.00
10	50.0	2.71	2.92	3.13	3.34	4.17	5.00
15	33.3	1.81	1.95	2.08	2.22	2.78	3.33
20	25.0	1.36	1.46	1.56	1.67	2.08	2.50
25	20.0	1.08	1.17	1.25	1.33	1.67	2.00
30	16.7	0.90	0.97	1.04	1.11	1.39	1.67
35	14.3	0.77	0.83	0.89	0.95	1.19	1.43
40	12.5	0.68	0.73	0.78	0.83	1.04	1.25

Summary.—The data in the previous paragraphs are general in character and do not strictly represent any particular plant, but they serve to illustrate the general relations between current density and cost of operation which have to be considered in designing an electrolytic plant.

The first step in such a design after determining the desired capacity of the proposed plant and the probable cost of power per kilowatt hour is to combine the data given under the various preceding headings and determine the approximate current density, thereby settling the size of the tank house and power plant.

As an illustration and without carrying such an analysis into the details necessary in actual work we will assume that the gain from released heat just offsets the loss from decreased current efficiency as the density is raised; that interest and depreciation on the tank house and power plant shall be 20 per cent per annum; that the silver and gold values in the anodes amount to $100 a ton; and that we are interested in five locations where the probable power cost is estimated at 1/10c., 1/4c., 1/2c., 3/4c. and 1c. per kilowatt-hour respectively, and other conditions are equal.

These assumptions are combined with the data from the several tables and diagrams in Table 18.

TABLE 18.—GENERAL RELATION BETWEEN CURRENT DENSITY AND COST

Current density	Kw.-hr per ton	$ Investment per ton-day	Cost in Dollars per Ton									Dollars per ton				
			Interest and depreciation	Metal interest	Metal loss	Labor	Power					Total operating cost				
							1/10c.	1/4c	1/2c.	3/4c.	1c.	1/10c.	1/4c.	1/2c.	3/4c.	1c.
5	104	7740	4.30	6.67	0.09	0.18	0.10	0.26	0.52	0.78	1.04	11.34	11.50	11.76	12.02	12.28
10	198	4360	2.42	3.34	0.25	0.24	0.20	0.50	0.99	1.49	1.98	6.45	6.75	7.24	7.74	8.23
15	290	3420	1.90	2.22	0.48	0.39	0.29	0.73	1.45	2.18	2.90	5.28	5.72	6.44	7.17	7.89
20	386	3140	1.74	1.67	0.75	0.46	0.39	0.97	1.93	2.90	3.86	5.01	5.59	6.55	7.52	8.48
25	480	3080	1.71	1.33	1.12	0.52	0.48	1.20	2.40	3.60	4.80	5.16	5.88	7.08	8.28	9.48
30	574	3140	1.74	1.11	1.60	0.57	0.57	1.44	2.87	4.31	5.74	5.59	6.46	7.89	9.33	10.76
35	668	3280	1.82	0.95	2.25	0.63	0.67	1.67	3.34	5.01	6.68	6.32	7.32	8.99	10.66	12.33
40	762	3440	1.91	0.83	3.00	0.70	0.76	1.91	3.81	5.72	7.62	7.19	8.34	10.24	12.15	14.05

The figures worked out for total costs are not the actual costs of refining, but simply totals which vary as the actual costs will when the density is varied. In order to find the density which will give the minimum cost for each power cost these results are plotted in Fig. 19.

In Fig. 20 the minima so determined are plotted against the current density and we have established the general relation already shown in Fig. 16 between current density and power cost.

It will be observed that the two curves for theory and practice agree well except at the lower power costs where practice runs at a higher current density than would be expected from our discussion.

This is due largely to the fact that although a certain density may show minimum cost a higher density may show maximum profits. For example suppose that a plant operates with power costing ¼c. per kilowatt hour at the density for lowest cost shown by our curve in Fig. 20 to be 18 amp. per square foot, and that the profit from refining is $3.00 per ton. If now the density be pushed up to 25 amp. a square foot the cost by Fig. 19 will be increased about $0.33 a ton and the profit per ton be cut to $2.67; but the increased density will allow the plant to treat 38 per cent more copper so that instead of $3.00 we make an equivalent of 1.38 by $2.67 or about $3.70, with less than proportionate increase in capital expense.

This argument is fallacious where we are designing a plant for a certain tonnage, as our calculations have shown that the $0.33 excess cost would pay more than 20 per cent on the increased investment to bring the density back to 18 amp. per square foot, but practically a plant after being put into operation is crowded by the steady annual growth in the production of copper and we may say is unable to keep up with this demand for capacity by extensions.

On the other hand where power is expensive this process of expansion receives a much earlier check than where it is

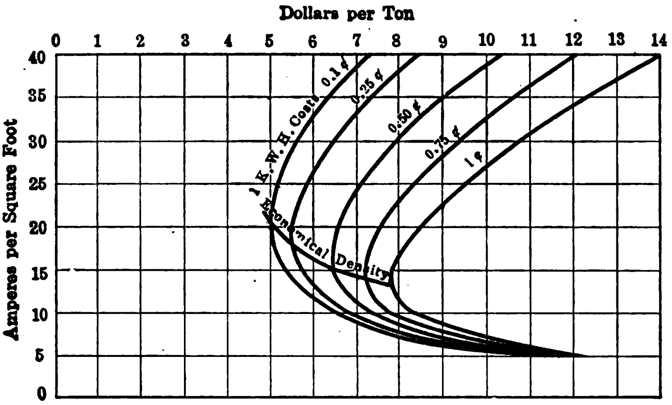

FIG. 19.—Current density *vs.* variation in total operating costs.

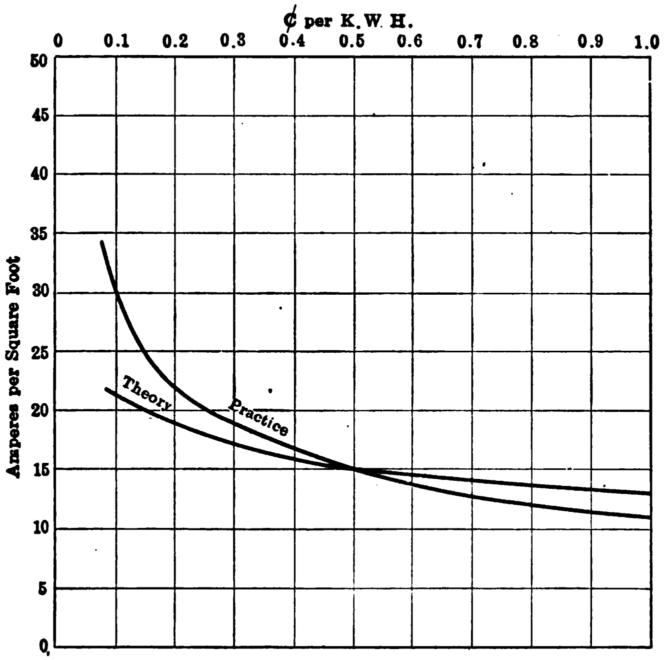

FIG. 20.—Current density *vs.* power cost—theory *vs.* practice.

cheap and this tends to explain at least part of the difference between theory and practice.

Then too at very low power costs we must be considering water power installations and this not only affects the investment factor we have assumed for steam plants, but introduces the question of secondary water power where excess power allowed to run to waste over a dam may be utilized at exceedingly low rates. Also the assumptions of interest rates, price of copper and silver and gold values have to be corrected for each practical case.

CHAPTER V

CURRENT EFFICIENCY

Current efficiency in an electrolytic operation is the ratio between the weight of product obtained per ampere hour and that called for by Faraday's law, for the current used in the desired reaction. It has therefore much to do with the cost of operations, but in this connection it must be considered jointly with the voltage factor; for example, the series system in copper refining operates at a lower current efficiency than the multiple and yet yields a greater weight of cathode per kilowatt-hour expended in the cell. For any given case, however, it is desirable to obtain as high a current efficiency as may be consistent with the cost of securing it, and it is our purpose to examine this question in its bearing to the multiple system of electrolytic copper refining.

The percentage which we obtain by dividing the weight in grams of cathode per ampere hour by 1.186 is less than 100 because part of the current performs no electrolytic operation on account of leakage or short circuits between electrodes, part is involved in reactions not desired and a portion of the cathode itself is redissolved chemically. It is even possible to obtain apparent efficiencies above 100 per cent under certain conditions.

In order to secure an exact correspondence with Faraday's law various niceties of operation must be observed and a great deal of study in this direction has been applied by those interested in voltameter measurements. It is quite possible, however, with care and dismissal of questions of labor cost, to obtain a working efficiency on a large scale of 99 per cent. Commercially it is found, however, that about 92 per cent is as high a figure as it is advisable to insist upon and at some plants 90 per cent or even 88 per cent is considered satisfactory. Current density has a direct bearing on the problem in that a high density greatly increases the difficulty in preventing short circuits between the electrodes.

The various factors involved may be classified as follows:

A. Current leakage:
  - a. To ground.
  - b. Through electrolyte.
  - c. Between electrodes.

B. Reaction:
  - a. Deposition of impurities.
  - b. Gassing.
  - c. Valence.

C. Cathode shrinkage:
  - a. Sulphatizing.
  - b. Ferric salts.
  - c. Nodules, etc.

A. CURRENT LEAKAGE

(a) To Ground.—The insulation resistance of the circuit from the ground may be determined by noting the reading of a high-resistance voltmeter when connected from either switch terminal on the live circuit to the ground by a simple application of Ohm's law. The current flowing through the voltmeter is obtained by dividing its reading by its known resistance; the total resistance in the leakage circuit is obtained by dividing the known line voltage by this current; the insulation resistance is found by subtracting the known voltmeter resistance.

It is evident that the resistance found in this way is a measure of the obstacles in the path of the current from the ground back through improper channels to the other leg of the circuit, and that by opening the main circuit at predetermined points and taking repeated measurements a leakage map could be worked out. This, however, should not be necessary, as while the insulation resistance of an electrolytic circuit will always be low—a usual value is five ohms—the actual loss of effective current from this source is a minor matter in any plant where the foundation piers are properly capped with glass plates and tank leaks kept from resulting in sulphate crystals climbing around promiscuously.

If we assume that a circuit has a total resistance of five ohms from one side to the other through the ground and that the line voltage is 150, this leakage will be but 30 amp. If the main current is 10,000 amp. and the leakage uniformly distributed so that it robs an average of but half the tanks, the percentage loss will be but 0.15 per cent.

(b) **Through Electrolyte.**—There are three ways of determining the loss of effective current due to improper shunt circuits through the circulation system: by direct measurement, by Ohm's law calculations and by Faraday's law calculations.

The direct method consists of placing carefully calibrated ammeters at various points in the circuit and comparing their readings, which would be identical except for losses under (*a*) and (*b*). Considerable care is required to avoid errors in measurement as thermoelectric effects may creep into the temporary shunt connections and magnetic errors, due to strong stray field, may distort the meter readings even when the instruments are protected by iron cases. An unprotected portable instrument may even be permanently thrown out of adjustment by exposure of its permanent magnets to the action of the stray field which exists within a couple of feet of a conductor carrying 10,000 amp.

Another method is to open the circuit in the center and note how many amperes are recorded by the power-house ammeter when full voltage is applied. This is not fair in that the voltage distribution throughout the circuit is not normal.

It will generally be found that the tanks at the far end of a circuit receive 3 or 4 per cent less than the switchboard current.

Ohm's law calculations may be made upon the liquid columns of electrolyte, as we know the resistance per cubic inch of the liquor, its physical dimensions and the voltages operating. Where the voltages are sufficiently low the lead pipe cannot act as a conductor, as when the current leaves it there must be sufficient voltage to decompose water. When such voltages occur sections of hard rubber or of rubber hose are employed to break the continuity of the metal path. It is also possible to take fall of potential readings along a lead pipe and figure the current flowing therein by Ohm's law and the specific resistance of hard lead.

Finally, we know that wherever the current enters the piping system it must deposit Faraday's equivalent of copper. This is of great practical assistance, as while it gives no information regarding the current flowing in the liquid itself, it does bring to daily attention any abnormal participation of the conduit system, and the accumulation of copper trees demands early attention to avoid stopping up the pipes.

The coating of lead sulphate which covers all tank linings and pipes exposed to the action of the electrolyte acts as an insulating paint of much value, as shown by the low efficiencies always obtained in starting up a new installation of bright tanks. A final insulating joint is usually effected where the electrolyte leaves a tank by allowing it to fall freely into the launder without a containing pipe for some inches.

Altogether ample means exist for measuring and controlling this source of loss.

(c) **Between Electrodes.**—The direct touching of anode and cathode is the most usual cause of poor efficiency. This condition can be brought about by the electrodes being carelessly spaced in the tank, by the curling of starting sheets, by falling of anode scrap, by omission of electrode insulators, by electrodes displaced sideways so as to touch the lead lining of the tank, by "treeing" of the cathode deposit, by the accumulation of an excessive quantity of slimes in the bottom of the tank or by the careless leaving of tools lying on top of the electrodes.

It is obvious that with the exception of "treeing" and falling anode scrap these causes may be removed in proportion to the amount of labor and inspection applied. Treeing involves the control of the cathode deposit by the choice of a suitable cathode age for the current density employed, adequate circulation of the electrolyte and the use of addition agents.

A cathode deposit starts as a fine frosting, and with a violent circulation this builds up with perfect smoothness. It is not possible to employ even a rapid circulation, however, on account of the consequent stirring up of anode slimes, and any mechanical scouring effect is therefore lost. On the other hand, the circulation must be maintained at a rate sufficient to supply copper ions at the cathode as fast as demanded by the current density, or other ions will act as carriers of the current and the deposit will become rough and non-adherent. Even under normal conditions fine needles soon spring out in crystal formation. The moment the cathode surface becomes roughened the parts nearest the anode offer the path of least resistance to the current and bad soon becomes worse.

The function of addition agents is first to round off these needles into blunt nodules, and second to change what is called "cocoa matting" structure to a hard compact deposit. Ordinary lubricating oil possesses some property which effects the first and minute quantities of glue the second.

The falling apart of scrap anodes results from incomplete refining of the blister copper in the anode furnace. As the condition causes an abnormal quantity of scrap and leaks from pierced tank linings as well as low-current efficiency the remedy lies in better furnace treatment.

A short circuit between two electrodes is not as serious as at first appears because there are a certain resistance due to conductors and contacts in series with each electrode and a number of parallel circuits. For example, if we have thirty pairs of electrodes and the series resistance amounts to one-quarter of the total across the tank, it is evident that a reduction of 75 per cent of the resistance in one of the thirty parallel circuits will but make it equal to four normal circuits out of the thirty and not draw any great share of the current. Then the increased current flow heats the conductors and contacts affected, and this increases their resistance. Finally, there is a certain rebate on the voltage side due to the lowered resistance of the tank when it comes to pounds of cathode per kilowatt-hour.

In general an economic balance is struck when about 5 per cent of the current is rendered non-effective by local short circuits.

B. REACTION

(a) **Deposition of Impurities.**—In the ordinary depositing tank the current consumed in the direct deposition of impurities is obviously negligible, as appears from the great purity of the cathode; in fact, it is an open question whether any of the traces of impurities found in cathode copper are due to electrolytic action. Where insoluble or partly soluble anodes are used and higher voltages obtain, this item becomes measurable. An example of the first case is where arsenic is deposited in a "liberator" tank in copper refining, and of the second where iron is deposited in a copper-nickel refinery.

(b) **Gassing.**—A copper cathode rarely shows upon analysis above 99.95 per cent copper. The metallic impurities may total 0.02 per cent, still leaving some unaccounted for difference. Part of this is included electrolyte, but after all allowances are made it seems probable that hydrogen is present either as hydride or by occlusion. We know that some addition agents harden the cathode, and that this hardness may be removed by annealing. When all the copper in a liquor is plated out, as in the case of an electrolytic assay, the gassing does not begin and the voltage rise suddenly upon the exhaustion of the copper, but some gassing starts early and the voltage gradually rises. In the same way local conditions at the cathode due to the moderate circulation employed may cause the separation of a certain amount of hydrogen at the cathode in a normally operating cell. It seems probable, therefore, that a small proportion of the current may be diverted into depositing hydrogen instead of copper, and even a minute quantity of hydrogen will account for a measurable current on account of its very low electro-chemical equivalent. For example, 0.03 per cent of hydrogen would take 0.9 per cent of the current. We do not know how much of a source of loss this condition is in straight copper work, but in nickel deposition it may be enormous, free hydrogen appearing in quantity at the cathode.

(c) **Valence.**—The efficiency is based upon the reaction

$$CuSO_4 + H_2O + \text{current} = Cu + H_2SO_4 + O$$

where copper acts as a divalent metal. It is evident that should the copper in the electrolyte be present in a cuprous salt, copper might be precipitated at an apparent efficiency of 200 per cent. Cuprous salts are undoubtedly formed to a certain extent at the anode, as shown by the cuprous chloride and metallic dust found in the slimes resulting from such a reaction as $Cu_2SO_4 = CuSO_4 + Cu$, although the latter is partly due to $Cu_2O + H_2SO_4 = CuSO_4 + H_2O + Cu$.

Cuprous sulphate is very unstable or we should gladly use it as the basis of an electrolyte, and it seems very unlikely that an appreciable amount exists at the cathode. The cuprous chloride found in the cathode when excess chlorides are allowed to accumulate in the electrolyte is doubtless due to direct reduction by the cathode as $CuCl_2 + Cu = 2CuCl$.

C. CATHODE SHRINKAGE

(a) **Sulphatizing.**—A certain amount of the deposited copper is redissolved by the electrolyte. While copper is not normally soluble in dilute sulphuric acid, the oxygen dissolved in the electrolyte aids in a slow attack—$Cu + H_2SO_4 + O = CuSO_4 + H_2O$ probably expresses the complete reaction. As would be expected the action is particularly marked at the solution line and various expedients, such as painting or changing the solution level, have to be employed in order to prevent the cathode loops cutting through at the solution line.

The amount of this chemical action is indicated by the growth in the copper content of the electrolyte after correcting for anode impurities dissolving electrolytically and cuprous oxide in the anode dissolving chemically, and it is found to increase rapidly with increase of temperature of the electrolyte.

A fair figure is about 2 per cent of the deposited copper, and if we assume that half of this came from the anodes we have an apparent loss in current efficiency of 1 per cent.

(b) **Ferric Salts.**—If the anodes are not free from iron, converter anodes, for instance, and the resulting ferrous sulphate is allowed to accumulate in the electrolyte, there is a tendency, increasing with concentration, for this salt to be oxidized at the anode—$2FeSO_4 + H_2SO_4 + O = Fe_2(SO_4)_3 + H_2O$. This is particularly the case in insoluble anode tanks where the ferrous sulphate acts as a true depolarizer. This ferric salt is again reduced, either electrically at the cathode—$Fe_2(SO_4)_3 + 2H = 2FeSO_4 + H_2SO_4$—or by the anodes and cathodes chemically—$Fe_2(SO_4)_3 + Cu = 2FeSO_4 + CuSO_4$. In either case there is a diversion of the current from its normal work and a corresponding loss in current efficiency. Under bad conditions, such as obtain in leaching copper ores, this loss may become very serious, but in straight refining work it should be entirely negligible.

(c) **Nodules, Etc.**—There is a certain apparent loss in efficiency due to mechanical shrinkage of the cathode from nodules falling into the slimes, chiefly due to inspection work on the tanks. This material is screened out of the slimes later, but is too contaminated to be considered legitimate production. Unless the deposit is rough the amount of this shrinkage will be but a small fraction of 1 per cent.

SUMMARY

The nine sources of efficiency loss are always present, but any or all of them can be kept down to a very small quantity. On the other hand, most of them may become very serious under undesirable conditions. In general we can say that entire disregard of conditions may result in an efficiency as low as 60 per cent, poor work 85 per cent, good balanced operating 92 per cent, and efficiency regardless of expense 99 per cent.

CHAPTER VI

IMPURITIES

Electrolytic refining gives a triple separation of the various impurities in a blister copper anode, distributed in the anode slimes, the electrolyte and the cathode. The chief object of the process is, of course, to make a pure cathode, and secondarily to keep impurities from mounting too high in the electrolyte, in order to keep the cost of purifying the electrolyte within reasonable limits. The ideal process would, therefore, send all of the impurities into the anode slimes, which would then be worked up into various by-products, and the electrolyte would stay of a constant composition. Practically a considerable proportion of the impurities dissolve in the acid sulphate electrolyte, and steps have to be taken for systematic purification of the solution.

Both the problem and the means of dealing with it have greatly changed in the last twenty years. Two decades ago, when electrolytic refining was in its infancy, there were large quantities of black copper to be treated, and many of the smelters were producing pig high in arsenic. An idea of this situation may be gained from some representative analyses of pig copper of that period, given in Table 19.

TABLE 19.—SOME PIG COPPERS ELECTROLYTICALLY REFINED IN 1901

Brand	Arsenic	Antimony	Iron	Sulphur	Lead	Copper
Argentine	0.46	0.40	0.03	0.15	....	96.5
Chicago	0.30	0.19	0.22	....	1.72	96.0
Germania	2.92	0.17	0.01	0.07	....	95.0
Philadelphia	0.86	0.08	None	Trace	....	96.2

This whole situation was changed when the strongly reducing action of the black copper furnace and the practically neutral atmosphere of the copper-producing reverberatory were supplanted by the strongly oxidizing Bessemer converter, and the widespread use of sulphur as a carrying agent for copper brought nearly the whole production through a process which efficiently removed most of the objectionable impurities.

On the other hand, some imported copper pig is of less than standard purity, and there is a steadily increasing production of secondary copper from plants treating junk by the old processes, and they often produce very foul pig. Some representative analyses of these various classes are given in Tables 20, 21 and 22.

Table 20.—Analyses of Some Examples of Secondary Pig

Brand	Arsenic	Antimony	Sulphur	Iron	Nickel	Lead	Copper
A	0.03	....	0.94	0.92	0.35	5.49	85.0
B	0.03	0.05	1.02	0.36	0.32	2.68	84.8
C	0.05	0.19	....	0.93	0.47	5.25	82.4
D	0.05	2.25	Trace	Trace	None	12.79	82.6
E	0.05	0.41	....	5.65	1.58	2.02	
F	0.05	2.63	0.75	5.53	0.33	2.36	84.9

Table 21.—Analyses of Some Foreign Pig Copper

Country	Arsenic	Antimony	Sulphur	Iron	Nickel	Lead	Copper
Chili.........	0.10	0.01	0.74	0.99	0.22	0.03	97.4
Japan........	0.18	0.12	0.39	0.03	0.06	0.83	97.6
Peru.........	0.13	0.20	....	0.03	Trace		
Spain........	0.11	....	0.69	1.03	0.02	0.13	97.7

TABLE 22.—ANALYSES OF NORMAL BLISTER COPPER

Country	Arsenic	Antimony	Sulphur	Iron	Nickel	Lead	Copper
Australia.....	0.001	0.011	0.224	0.029	0.047	0.003	99.30
Canada.......	0.037	0.045	0.090	0.050	0.411	0.002	98.80
Mexico.......	0.017	.....	0.260	......	0.040		
South America	0.007	.....	0.188	0.037	0.044	0.028	99.20
United States.	0.008	0.006	0.045	0.034	0.037	0.007	99.30

We have, therefore, the general problems of keeping the impurities out of the refined copper and of working up such of the impurities fom the anode slimes and the electrolyte as may show a commercial profit.

The early refineries had much trouble with even the first leg of this proposition, and the uncertainty as to the chemical purity of electrolytic copper produced in the early days had much to do with the premium established in favor of Lake Copper. Arsenic was the chief enemy, and its elimination from the electrolyte became the main metallurgical problem of the plant.

This situation brought about the development of a by-product bluestone plant, fed by systematic withdrawals from the electrolyte, the final mother liquors being precipitated upon iron and discarded.

Then the flood of incoming arsenic abated, and in some cases nickel became the major impurity, bringing about the development of the by-product nickel sulphate plant, the mother liquors being returned to the electrolyte.

In general, one of these two methods of control of the composition of the electrolyte have been used, and they will be examined more or less in detail later on.

The anode slimes were at first cupelled with lead, and only the silver and gold recovered, these being parted by sulphuric acid. Later, lead practice was discarded, except by those plants operated in conjunction with a lead refinery, and much work has been done upon the recovery of selenium, tellurium, platinum, palladium, arsenic, antimony, bismuth, etc. A quite complicated pyro-metallurgy, followed by electrolytic parting, has been developed, and much research devoted to the possibilities of a full wet process.

A discussion of the general question of impurities, therefore, falls under six main headings, namely: (A) sources, (B) exits, (C) distribution, (D) chemical requirements of refined copper, (E) recovery of soluble impurities from the electrolyte, and (F) recovery of insoluble impurities from the anode slimes.

A. SOURCES

Apart from the entering pig copper there are as many sources of impurities as there are supplies entering the process. While, of course, many of these sources are quite negligible, some are of sufficient magnitude to be worthy of consideration. Among these are fuel, fluxes and acids.

Fuel enters the process at various stages, but the only place where it is of account in this discussion is in the melting of cathodes. Here the various products of combustion and particularly the sulphur have to be reckoned with, as sulphur is one of the principal impurities in refined copper. The discussion of this question falls more normally under the head of chemical impurities in refined copper.

Fluxes include, by a somewhat liberal definition of the word, the materials of which the furnaces are made insofar as they enter the metallurgical slags, the true fluxes, such as limestone and pyrites cinder added in the retreatment of these slags, the charcoal or other carbonaceous covering used to protect molten copper from undue oxidation, bone ash or similar material used to "butter" the molds, and soda nitre and soda ash used as fluxes chiefly in the treatment of the anode slimes, and the antimonial lead with which the tanks are lined.

Under acids we have sulphuric, nitric and hydrochloric, the last sometimes as sodium chloride. The sulphuric acid is added to make up losses of free acid in the electrolyte in the copper electrolysis and the nitric similarly in the parting plant. The chloride is added to the copper electrolyte chiefly to precipitate antimony as oxychloride, although it has been claimed by many to have positive value as an addition agent.

Fortunately most of these process supplies carry but little in the way of metallurgical impurities. The notable exceptions are blast-furnace fluxes, sodium salts and sulphuric acid.

As refinery slags are made by a union of metallic bases with siliceous furnace material, it is necessary to find lime and iron to replace the copper in these slags. The natural source of iron in the vicinity of most refineries is pyrites cinder resulting from the manufacture of sulphuric acid. As arsenic is commonly associated to a greater or less degree with iron pyrites, more or less of this element may be introduced in this manner.

In the same way sulphuric acid made by burning pyrites is likely to contain considerable quantities of arsenic as an impurity, and unless purified acid is used it may be a heavy contaminating agency, since where sulphate salts are made as a by-product the acid purchases are large.

In like manner any nitrate of soda used in the silver building boiling tanks as an oxidizing agent or sodium chloride added to the electrolyte directly bring about a concentration of sodium sulphate which may be objectionable.

B. EXITS

A complete analysis of what may be called "exits" for impurities has been given in Chapter I. Based on this, eliminating such items as do not bear directly on our immediate problem, we may classify the exits as (*a*) outgoing commercial products, (*b*) slags and (*c*) stack gases.

The ideal process would eliminate the two latter products entirely and send all of the impurities out as commercial products. Practically not only do several elements escape in their entirety, but excepting copper, silver and gold, the remaining are recovered at far from 100 per cent efficiency.

The tendency to-day is to check stack losses so that in time there will be but two outlets, the one to commerce and the other to the slag dump.

When markets are unsatisfactory some of the products can be stored, as has already been the case with selenium, tellurium and bismuth.

C. DISTRIBUTION

The distribution of impurities depends partly upon their chemical characteristics and partly upon the metallurgical practice of the individual plant.

In the first place, the cathode will contain measurable quantities of all impurities found in the anodes, although there is room for some discussion as to what proportions of these arrive by electrolytic deposition, by inclusion of electrolyte and by mechanical contamination by anode slimes.[1] The percentage of anpde impurities found in the refined copper may be seen by direct comparison of average analyses over a long period of operation, as in Table 23.

TABLE 23.—METALLURGICAL EFFICIENCY OF REFINING

Element	Anode	Wirebar	Per cent of original impurity	Efficiency of refining
Copper	99.030	99.939		
Silver	0.1687	0.00131	0.78	99.22
Gold	0.0051	0.000013	0.25	99.75
Sulphur	0.0075	0.0029	38.60	61.40
Nickel	0.3200	0.0037	1.15	98.85
Lead	0.0567	0.0020	3.52	96.48
Arsenic	0.0523	0.0015	2.87	97.13
Antimony	0.0409	0.0034	8.32	91.68
Bismuth	0.0051	Trace		
Tellurium	0.0282	0.00015	0.53	99.47
Selenium	0.0682	0.00040	0.59	99.41
Iron	0.0181	0.0039	21.55	78.45

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[1] See Addicks: *Trans.* Am. Electrochem. Soc., vol. xxvi, p. 51.

The four elements showing a cathode recovery of over 99 per cent are silver, gold, selenium and tellurium, none of which dissolve in the electrolyte. Therefore, the mechanical contamination by anode slimes is less than 1 per cent. Then we have nickel at 1.15 per cent; this element, while present in oxidized form in the slimes, goes chiefly into solution as sulphate. The same is true of arsenic which, however, forms a light slime which readily attaches itself to the cathode. Lead comes not only from the anodes but from the tank linings, so that the efficiency is not quite true in this case. The same is true in lesser degree of antimony, as hard lead is universally used to-day for tank linings. Antimony is further precipitated from the electrolyte as oxychloride, as previously described, entering the float slime. A characteristic analysis of this sediment is given in Table 24.

TABLE 24.—ANALYSIS OF FLOAT SLIME

Element	Per cent
Copper	3.0
Arsenic	13.0
Antimony	30.0
Bismuth	8.0
Silver	4.0
Iron	0.3

When we come to consider the efficiency of refining with regard to iron and sulphur we must remember that both these elements are introduced in the melting of the cathodes, the former in the rabbles and tools used and the latter in the fuel and ladle charcoal, and we also have sulphate sulphur from the electrolyte, so that the figures are misleading.

We may say in a general way, therefore, that the efficiency of refining is very high and that the cathode copper offers a very small outlet for anode impurities; further, that the great bulk of those impurities which are soluble in dilute sulphuric acid will concentrate in the electrolyte.

The balance of the impurities must go into the slimes and we can attempt a measure of this by comparing the assays of the anodes and of the raw slimes as they come from the tanks except for boiling free of soluble salts. This is done in Table 25.

TABLE 25.—CONCENTRATION OF ANODE IMPURITIES IN SLIMES

Element	Anode, per cent	Slimes, per cent	Per cent anodes × 84.4	Per cent recovered
Copper	98.14	14.3		
Silver	0.417	35.0	35.2	99.5
Gold	0.00711	0.643	0.600	(107)
Nickel	0.314	5.25	26.5	19.8
Arsenic	0.236	2.68	19.9	13.5
Antimony	0.0906	5.35	7.6	70.0
Bismuth	0.0088	0.46	0.74	61.9
Sulphur	0.0037	1.69	0.31	(541)
Iron	0.0123	0.17	1.04	16.4
Lead	0.0456	2.44	3.85	63.4
Selenium	0.0479	5.70	4.04	(141)
Tellurium	0.0318	2.69	2.68	(100)
Zinc	0.0100	Trace	0.84	None
Insoluble	0.1213	6.60	10.2	64.5

The last two columns of Table 25 assume that 99.5 per cent of the silver was in the slimes the remaining 0.5 per cent being in the cathodes. On this basis the recovery in the slimes of the remaining elements has been calculated. Of course, the gold, selenium and tellurium should also show a recovery of about 99.5 per cent, and the discrepancies simply indicate that the correspondence between identity of slimes and anodes is not quite exact.

The sulphur shows a large excess due to the fact that the sulphur in the sulphuric acid of the electrolyte has combined with some of the impurities as sulphates which have not proved readily soluble.

Nickel, iron, zinc and arsenic, as would be expected, show small recoveries; the first three form readily soluble sulphates and arsenious acid is quite soluble in the electrolyte. Nevertheless, with the exception of zinc the slimes retain some of even these elements.

Lead which has a but slightly soluble sulphate, antimony, which is precipitated as oxychloride, bismuth and siliceous matter show high but not perfect recoveries.

Much of this group goes into the float slime which is largely separated out before the heavy slimes are sent to the silver building and this, if corrected for, would make a nearly complete slime recovery.

An analysis of the electrolyte corresponding to the example given above would be about as stated in Table 26.

TABLE 26.—REPRESENTATIVE ANALYSIS OF ELECTROLYTE

Specific gravity	1.226
Per cent free acid	12.03
Per cent copper	2.94
Per cent nickel	1.48
Per cent chlorine	0.0031
Per cent arsenic	0.916
Per cent antimony	0.0350
Per cent iron	0.060
Per cent bismuth	0.0026
Per cent zinc	0.0166
Per cent alumina	0.0595
Per cent calcium sulphate	0.1348
Per cent magnesium sulphate	0.0370
Per cent sodium sulphate	0.5048

A comparison of the relative values of the impurities in the electrolyte with those in the anodes confirms in a general way the distribution already shown. It is evident that in this particular case nickel is the controlling impurity and that any system of purification of the electrolyte which will hold this element at the desired concentration will automatically take care of arsenic and other impurities.

That the degree of concentration of soluble impurities in the electrolyte has a direct bearing upon the purity of the cathode product may readily be proved in the cases of arsenic and nickel. Tables 27 and 28 give comparisons of wirebar content of arsenic and nickel with corresponding

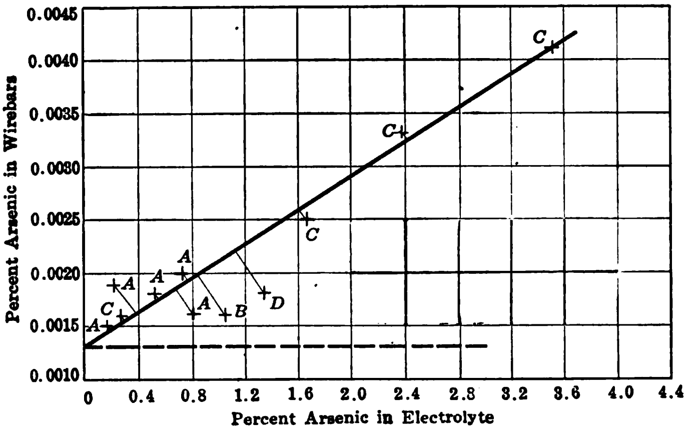

FIG. 21.—Arsenic in electrolyte *vs.* arsenic in wirebars.

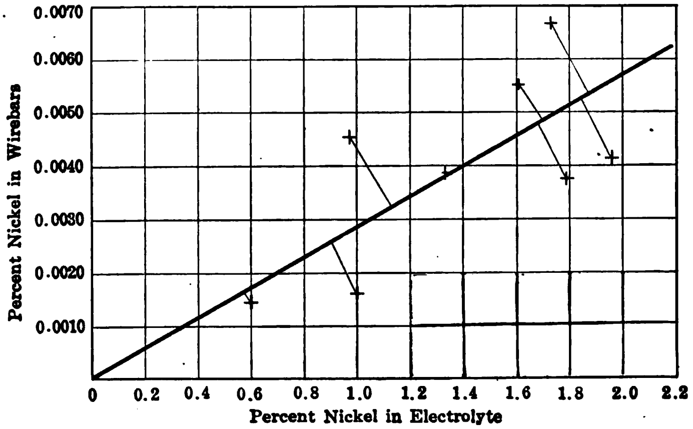

FIG. 22.—Nickel in electrolyte *vs.* nickel in wirebars.

analyses of electrolyte at a number of plants. These data are plotted in Figs. 21 and 22. In the case of arsenic the line cuts the zero ordinate at 0.0013 per cent indicating this quantity due to contamination by slimes.

TABLE 27

Plant	Representing	Per cent As in electrolyte	Per cent As in wirebars
A	1909	0.728	0.0020
A	1910	0.789	0.0016
A	1911	0.506	0.0018
A	1912	0.219	0.0019
A	1913	0.194	0.0015
B	21 Months	1.04	0.0016
C	1 Lot	0.25	0.0016
C	5 Lots	1.64	0.0025
C	4 Lots	2.37	0.0033
C	3 Lots	3.55	0.0041
D	25 Months	1.34	0.0018

TABLE 28

Plant	Representing	Per cent Ni in electrolyte	Per cent Ni in wirebars
A	1909	1.95	0.0041
A	1910	1.60	0.0055
A	1911	1.73	0.0066
A	1912	1.32	0.0038
A	1913	1.78	0.0037
B	10 Months	0.973	0.0045
C	Rough figures	1.00	0.0016
D	1 Lot	0.594	0.0014

D. THE REQUIREMENTS OF REFINED COPPER

This subject is of sufficient importance to be reserved for treatment at length in Chapter IX.

E. PURIFICATION OF THE ELECTROLYTE

Any system of purification must regularly withdraw sufficient electrolyte to control the amount of the chief impurity. For example, in the analysis given in Table 26 nickel is the element which would first grow to undesirable concentration, although arsenic is a close second and the maximum allowable values of various elements depend upon conditions under which an individual plant is operating. Both nickel and arsenic have been allowed to reach 3 per cent in the electrolyte without disaster in certain local and temporary cases. The first thing is therefore to ascertain what quantity of electrolyte must be daily withdrawn.

I. Purification by Cementation upon Iron.—The early methods of purification consisted simply in cementing the copper upon iron and throwing the copper-free liquor away. The scrap iron would be piled in a lead-lined tank, the liquor run in and brought to a boil by heating with steam and at the end of an hour a bright iron rod would not tarnish when introduced, indicating complete precipitation of the copper. The liquor was then run to the sewer and occasional clean-ups of cement copper made.

Theoretically but 0.88 lb. of iron is required to replace one pound of copper. Generally, however, the scrap contains more or less inert graphite and iron oxide, the iron precipitates more or less arsenic, etc., and the high free sulphuric acid actively attacks the iron so that as much as two pounds of scrap iron are often required per pound of copper precipitate.

The cement is generally quite foul running about as shown in Table 29:

TABLE 29.—ANALYSIS OF TYPICAL CEMENT FROM DISCARDED ELECTROLYTE

Copper, per cent	Iron per cent	Arsenic, per cent	Silver, oz. per ton	Gold, oz. per ton
70	5	10	15	0.1

The silver and gold come, of course, from suspended slimes carried over from the electrolytic tanks.

While this method has the advantages of simplicity in operation and small plant required, it makes a foul cement which requires retreatment, runs up a heavy bill for scrap iron and entirely wastes both the free and combined sulphuric acid content of the electrolyte.

Nevertheless, it is still used in some small plants, and is always considered a legitimate emergency measure for dealing with a bad electrolyte.

II. The By-product Manufacture of Bluestone.—The next purification method developed was to go into the manufacture of commercial bluestone, using electrolyte as a raw material. The process consisted of four steps, as shown in Fig. 23: Neutralization of free acid by means of anode copper, concentration of neutral liquor by boiling, crystallization of heavy liquor, and cementation of mother liquors.

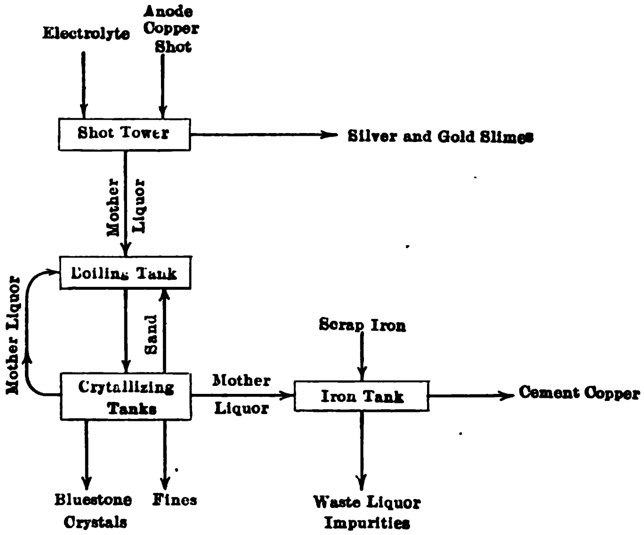
Electrolyte
Anode Copper Shot
Shot Tower
Silver and Gold Slimes
Mother Liquor
Boiling Tank
Mother Liquor
Sand
Scrap Iron
Crytallizing Tanks
Mother Liquor
Iron Tank
Cement Copper
Bluestone Crystals
Fines
Waste Liquor Impurities

FIG. 23.—Flow-sheet of by-product bluestone plant.

In this way the entire free acid content as well as that already combined with copper in the electrolyte is recovered as sulphate of copper except that discarded in the final mother liquors and the iron tanks do not receive any liquor until the impurities have risen to a point where bluestone of commercial purity can no longer be made by fractional crystallization.

Also, as anode copper is used for neutralizing the free acid a certain amount of copper is refined, the silver and gold remaining as slime in the shot towers, and therefore the by-product plant is entitled to a certain amount of tolls to be credited against its operating expense.

Then there is still the legitimate profit from the market price of bluetone, so that it is possible to place the purification system on a revenue-producing basis.

On the other hand, the plant required is bulky, it is dependent for results upon the market for bluestone which at times is badly overproduced and finally the plant is strictly limited to a predetermined capacity, and therefore uses the electrolyte as a reservoir for fluctuating amounts of anode impurities. Also where very foul anodes are to be treated the bluestone plant becomes enormous.

However, as this system is more or less used to-day, though generally in addition to other methods, some account of the process will be given.

1. *Capacity.*—A building 50 ft. by 150 ft. ground plan will produce about 140,000 lb. of bluestone a month. This is equivalent to about 35,000 lb. of copper, but about three-quarters of this comes from the shot copper and only 9000 lb. is from the electrolyte, so that this plant would represent the withdrawal of but 100 cubic feet a day of electrolyte.

2. *Shot Towers.*—Copper is not readily soluble in dilute sulphuric acid, especially in the presence of various impurities. In order to promote the rate of solution the liquor is heated and poured over the copper intermittently so as to promote the oxidation of the copper. The towers are built in various ways in order to accomplish this, but the simplest method is to spray the hot liquor over the top of the bed and let it trickle through.

The copper itself is cast in the form of so-called shot in order to increase the surface exposed. Shot is a mass of small hollow irregular spheres, and as these dissolve away, the mass crumbles and this tends to prevent packing. It is made by adding a little matte to an anode furnace charge to lower the pitch and then pouring a thin stream of metal through a blast of air into a well filled with water. More or less minor explosions occur, but if the procedure is skillfully carried out the result is a surprisingly light mass of detached globules ranging from 1/4 in. to 1 1/2 in. in diameter.

Underneath the shot towers is a well, and here the silver and gold slimes wash down as the copper is dissolved and settle out. These are periodically collected and sent to the silver refinery to be smelted along with the anode slimes from the electrolytic tank house. It is impossible absolutely to neutralize the free acid in the electrolyte in this way in a reasonable time, but by repeated circulation at high temperature it is possible to bring it below 1 per cent. The temperature must be above 150°F. for effective work, and the time required is from four to seven days in a plain tower.

3. *Boiling Tanks.*—The boiling tanks are lead-lined open tanks with closed steam coils and the liquors from the shot towers are here concentrated as far as steam at a reasonable pressure for lead pipes will carry them. This is about 38° Beaumé and corresponds to 9 or 10 per cent copper. The time required for a batch is about eight hours.

4. *Crystallizing Tanks.*—The crystallizing tanks are shallow, open, lead-lined tanks provided with strips of lead hung from cross bars on which the crystals grow. The liquor from the boiling tanks is allowed to stand quiescent in these tanks for five days, which time experience has shown to be the best. A longer period results in more or less resolution, while forced cooling by means of cooling coils results in a crop of small and less pure crystals.

The choice large crystals grow chiefly as trees on the lead strips. At the bottom of the tanks a mass of fine crystals forms.

The crystals are removed after the mother liquor has been pumped out and are then generally dried by hot air and screened to separate the coarse and fine, each class being packed in barrels for shipment. The fine sand is sent back to the boiling tanks and recrystallized.

The best crystals physically are made from truly neutral liquor. Should the liquor carry 2 per cent acid or over, the crystals are likely to be hygroscopic and are not a prime market product. Also calcium sulphate, if present in the liquor to any extent (this salt is sparsely soluble in such solutions), will form white "whiskers" on the crystals.

The main physical question is, therefore, to obtain a maximum proportion of large, clean, dry crystals. An ordinary yield is 47 per cent large crystals, 9 per cent pea and 44 per cent sand.

Chemically the problem is to keep the mother liquor down in impurities to a point where fractional crystallization is sharp enough to make a commercial salt. The alternative is to dissolve and recrystallize. The effect of recrystallizing is shown in Table 30, where "bottoms" have been dissolved and crystallized, forming crystals and a second crop of bottoms, but leaving most of the arsenic and antimony behind in the new mother liquor.

TABLE 30.—REMOVAL OF IMPURITIES FROM BLUESTONE BY RECRYSTALLIZATION

	Per cent arsenic	Per cent antimony
Original "bottoms"	0.434	0.113
New crystals	0.076	0.013
New bottoms	0.117	0.014

$CuSO_4.5H_2O$ contains approximately 25.4 per cent copper, 38.5 per cent combined acid and 36.1 per cent water of crystallization. Ninety-nine per cent crystal should, therefore, run slightly better than 25 per cent copper and 98 per cent slightly less and bluestone is generally considered to carry one-quarter copper. In Table 31 are given some random analyses of the products from several plants.

TABLE 31.—REPRESENTATIVE ANALYSES OF BLUESTONE

Source	Remarks	Per cent copper	Per cent iron	Per cent nickel	Per cent arsenic	Per cent antimony
A	Coarse........	24.97	0.195	0.358	0.018	0.006
A	Fines.........	24.72	0.215	0.419	0.040	0.009
A	Seconds.......	23.25	0.250	1.250	0.090	0.017
B	"Anhydrous"	26.18	0.600	1.850	0.668	0.030
C	Coarse........	25.22	0.025	0.150	0.003	0.005
D	Coarse........	24.80	Trace	.....	0.150	0.018

The wide range of the impurities in the different products in Table 31 is due chiefly to the difference in the electrolytes at the various plants. The salt showing 26.18 per cent copper had been overdried, thereby losing some of the water of crystallization; this makes a dirty white crystal and is also a source of loss to the producer, as copper contents above the guaranteed amount are not paid for.

5. *Mother Liquors.*—The mother liquor from the crystallizing tanks are returned to the boiling tanks and reconcentrated with fresh liquor from the shot towers. As the impurities grow in concentration, however, the bluestone is increasingly contaminated and a point is reached where a proportion has to be diverted to the iron tanks to be worked up into cement copper.

Sometimes a foul copper-nickel-iron sulphate is crystallized from such liquors before cementing. An example of such a salt is shown in Table 32.

TABLE 32.—COPPER, NICKEL, IRON SULPHATE FROM MOTHER LIQUOR

Per cent copper	Per cent nickel	Per cent iron	Per cent arsenic	Per cent antimony	Oz. per ton silver
9.52	11.50	1.19	0.23	0.024	0.15

The silver is, of course, due to contamination by suspended slimes from the shot towers. Similar quantities and a proportionate amount of gold is found in bluestone when anode copper is used for shot. A salt of this character has no commercial use, but is a good starting point for nickel recovery as another by-product.

III. Purifying With Insoluble Anode Tanks.—Where but little nickel is present and arsenic is the predominant impurity, a simple process based upon the use of insoluble anode tanks is sometimes employed.

A certain amount of electrolyte is diverted to a set of tanks provided with lead anodes and operating in cascade so that practically all of the copper and arsenic are plated out and the equivalent sulphuric acid is liberated. The treated liquor is returned to the electrolyte.

This uses a considerable amount of power, but recovers the acid and calls for no scrap iron. It takes three tanks in cascade to bring the copper and arsenic down to 0.1 per cent or less. The first tank will operate at about 85 per cent current efficiency and produce cathodes, which may with reasonable safety be included in the fine copper output; the second will run at perhaps 50 per cent efficiency and the cathodes reserved for casting copper or anode changes; the last tank runs at a very low copper efficiency and produces a sludge consisting of about half copper and half metallic arsenic. Much of the latter can be eliminated from this by roasting and sublimation, if desired. Such insoluble anode tanks evolve arseniuretted hydrogen, which is very poisonous, and they should therefore be located out of doors.

This method is limited by the permissible amount of impoverishment of the electrolyte in copper; if carried to extremes it is evident that the whole copper content of the electrolyte would be withdrawn, the acid being correspondingly increased. On the other hand, when nickel is practically absent from the anodes and the copper withdrawals necessary to hold down the arsenic do not exceed the normal growth of copper in the electrolyte, it is a satisfactory solution of the purification problem.

IV. Complete Cyclical Purification.—The method of purification of the electrolyte in general use among copper refineries to-day is shown in diagrammatic form in Fig. 24. Electrolyte is diverted to insoluble anode tanks at a rate just sufficient to keep the determining impurity at the desired point. This impurity is almost always nickel or arsenic and generally the former.

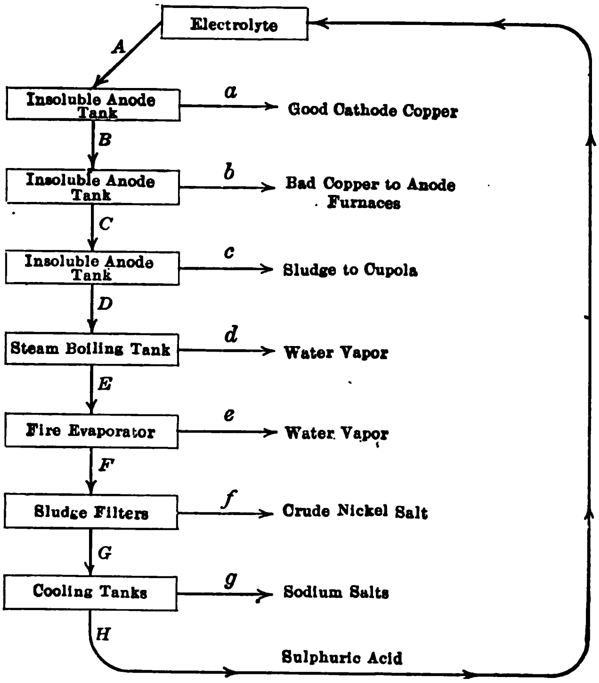
Electrolyte
A
Insoluble Anode Tank
a
Good Cathode Copper
B
Insoluble Anode Tank
b
Bad Copper to Anode Furnaces
C
Insoluble Anode Tank
c
Sludge to Cupola
D
Steam Boiling Tank
d
Water Vapor
E
Fire Evaporator
e
Water Vapor
F
Sludge Filters
f
Crude Nickel Salt
G
Cooling Tanks
g
Sodium Salts
H
Sulphuric Acid

FIG. 24.—Modern method of purifying electrolyte.

The first step in the process is the same, therefore, as that just described in the preceding paragraph, but the liquor resulting therefrom instead of being returned to the electrolyte is sent to a steam boiling tank where it is concentrated as in the manufacture of bluestone up to about 40° Beaumé.

The liquor is then transferred to a tank made of boiler plate, as, being nearly copper-free and of high sulphuric acid content, it is no longer seriously corrosive to iron. This evaporator is heated by direct fire until the syrup reaches about 70° Beaumé, at which strength practically all the impurities except the small amount of arsenic which has escaped the insoluble anode tanks and the sodium and potassium salts have been precipitated as anhydrous sulphates.

This heavy liquor with its suspended solids is then tapped on to a sand filter where the bulk of the strong acid is filtered out. The mushy salts are then shoveled on to a draining board and finally into a sucking tub, where the acid is displaced with a very small quantity of water.

The partly washed salts are then shoveled on to a drying floor where the water is gradually taken up as water of crystallization and the mass sets into lumps of partially hydrated sulphate, which may be readily handled and shipped and is in good physical shape for charging into a furnace for the recovery of metal values.

If the strong acid filtrate is chilled before returning it to the electrolyte much of the sodium sulphate will be thrown out. Practically this occurs at ordinary winter temperatures at most of the plants.

This process is completely cyclical except for the combined acid sent out with the crude nickel salts and such acid losses as may be incurred by fumes from the fire evaporator. The nickel is recovered in a form reasonably acceptable to a nickel smelter; but little low-grade cathode copper is made, and the arsenic could be separately recovered were it worth while to do so.

The objection still applies that the electrolyte may be robbed of too much copper and this has especial force when discussing nickel, as much of the anode nickel appears to dissolve electrochemically so that more copper is plated out at the cathode than is electrochemically dissolved at the anode.

The remedy, in case of trouble of this character, is to build shot towers and allow a certain proportion of the regular electrolyte to trickle through them. As the solution so diverted has always high free acid content, such towers are more active than in a bluestone plant, where complete neutralization is the object.

The chemical separations are not sharp and some leeway has to be left for circulating impurities due to this fact. An example of crude nickel salt made in this way is given in Table 33.

TABLE 33.—ANALYSIS OF CRUDE NICKEL SALT

Per cent water	Per cent copper	Per cent iron	Per cent nickel	Per cent arsenic
17.0	0.57	1.76	28.45	0.02

F. RECOVERY OF INSOLUBLE IMPURITIES FROM THE ANODE SLIMES

This question involves the whole metallurgy of the silver refinery and will be taken up separately in the next chapter.

CHAPTER VII

BY-PRODUCTS

In the last chapter the various elements commonly associated with copper were discussed as impurities and their treatment carried far enough to get them out of the refined copper. We therefore left them as anode slimes and purifying plant salts or as furnace slags and flue dust. We have now to discuss the working up of these impure metallurgical products into marketable materials.

Market.—We may broadly divide the possible by-products into three main classes as to their probable disposition as: First, those which are readily marketable in any quantity which such sources are ever likely to supply; second, those which have a limited and therefore sensitive and widely fluctuating market, and, third, those which have at the present time practically no market at all. These groups consist of the following: first, gold, silver, platinum, palladium, lead, nickel and antimony; second, bismuth, arsenic, cobalt, selenium; and, third, tellurium.

Palladium is the only uncommon member of class one. The production of this element is as yet quite small and this amount is readily absorbed by the jewelry and scientific-instrument trade. Practically it has the useful qualities of platinum, but is of about half the density.

Bismuth goes chiefly into the drug trade. Any large production of it floods the market and depresses the price. It is seldom associated with copper in any quantity, although it is the mainstay of electrolytic lead refining.

There is a large market for *arsenic*, which is used chiefly for its poisonous properties in insecticides, etc., but in recent years the great output of arsenious oxide recovered from smelter flue dusts has glutted this.

Cobalt is an element that has not yet found itself. The Canadian Government has conducted a wide investigation as to its possible uses, but aside from the use of cobalt oxide in the manufacture of smalt and for whitening yellow pottery and the use of the metal to give certain minor properties to cobalt-plated ware and cobalt alloys, no marked characteristic giving it a superior value to nickel has been discovered, and so far it has not been found possible to produce it at the price of nickel. Except in one or two notable cases, as in Katanga bullion, cobalt is not associated with copper to any extent.

Selenium was a rare element a few years ago; to-day a single copper refinery could easily produce ten tons a month, could it be marketed. Its peculiar photo-electric property has not created any tonnage demand, and its only major use is for coloring ruby glass. This creates a steady but very moderate market.

Tellurium could also be produced by the ton, but there appears to be no reasonably extensive market for it. The various plants producing selenium and tellurium are now joining trying to develop wider markets for these elements by scientific research.[1]

Market Requirements.—*Gold* is nearly always sold to the United States Assay Office. There are no requirements as to fineness, but the bullion is weighed, sampled and assayed by the Government. It is then purchased with a "gold check" on the Treasury Department for full value less certain refining charges. These charges are so adjusted that they are greater than those of an outside refiner, unless the gold is nearly pure; but the last traces of impurities are taken out by the government for less than it would cost others who are properly equipped. This is due to the fact that the government is not concerned with interest charges while the gold is in process, while the individual is very much concerned therewith. The result is that it is customary for the refiner to bring his gold up to perhaps 985 parts fine, the balance being chiefly silver (which is not paid for above 992) and sometimes small quantities of the platinum group of metals which are likewise forfeited.

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[1] See Lenher, *Chem. & Met. Eng.*, vol. 22, p. 1108.

Silver is at times exported to London when the English market is higher than the American by an amount sufficient to pay transfer charges. America also makes direct shipments westward to the market in the Orient.

The silver used locally goes to brokers, but little of the home consumption passing directly into the hands of the user.

The chief impurity in bar-silver is copper. For the American market it is customary to produce 999 fine, and for the English 998. As value over 998 is neglected in payments from abroad while penalties are exacted if it runs under that point, care must be taken to bring high grade electrolytic silver *down* in fineness. This is done when melting by the addition of copper wire in sufficient quantity to allow a safe margin above 998 for assay variations. Also, as only even quarter ounces are paid for it is customary to plug the bars with silver to a safe weight above an even quarter. The same result could be obtained by trimming but this would obscure any evidence of theft by trimming in transit.

Tellurium is the main metallurgical enemy of silver and must be thoroughly eliminated from it in order to prevent brittleness in subsequent rolling of the metal.

Printed schedules of the charges of the U. S. Mints and Assay Offices are periodically issued by the Treasury Department and may be obtained upon application. The points of chief interest to a copper refiner in the schedule in effect July 1, 1919, are: first, all deposits are subject to a melting charge of $1 per 1000 oz.; second, ordinary doré is charged ½ cent an ounce for parting and refining; third, gold bullion between 950 and 991.75 parts fine is charged 2 cents an ounce for refining while silver contents in such bullion above 992 fine are not paid for; fourth, metals of the platinum group are not paid for, although their presence in quantity will be reported for the information of the depositor, and fifth, government weights and assays control, the weights being to one hundredth of an ounce and the fineness to the nearest quarter-part.

The *platinum group* of metals are sold as a rule in crude shape as a sponge or powder, running 950 fine or better. In passing, it may be of interest to state that the ordinary assay methods for the platinum group give very inaccurate results and that a true assay for platinum and palladium is a tedious and costly operation, involving repeated precipitations in order to free the platinum metals from the last traces of lead sulphate and silver chloride.

Lead is seldom present in any quantity unless it is added in the cupeling operation in the silver refinery. Its market requirements are too well known to need discussion here.

Nickel is used first, as nickel sulfate or as a double ammonium sulfate in nickel plating; second, as anodes; and third, as shot or oxide for steel alloying. The crude sulphate of nickel, iron and copper produced by a purifying plant can be made into a reasonably pure sulphate by wet methods. This is then broken down by heat into oxide which is in turn reduced by carbon to metallic nickel in an electric crucible. Carbon-free nickel can be made electrolytically from this product if desired. Nickel anodes are generally alloyed with more or less iron, although conditions in the trade are improving in this respect with a corresponding improvement in the character of nickel plating. The production of pure nickel salts is very troublesome and should not be attempted unless unusually pure electrolyte is available as a starting point. One of the large manufacturers of this product had so much trouble in meeting the strict requirements of the trade that wet methods of production were abandoned and the salt produced by dissolving pure nickel.

Electrolytic nickel should run 99.80 nickel plus cobalt and should be free from carbon and oxides. The cobalt should not exceed 0.3 per cent and the sulphur should be very low. Small quantities of iron and copper are permissible and a little arsenic is generally present.

Table 34 gives some examples of the crude by-product salt as made by the refinery which is the raw material for by-product nickel; also analyses of commercial single and double salts as found in the market.

TABLE 34.—ANALYSES OF NICKEL SALTS

Source	Type	Per cent Ni	Per cent Cu	Per cent Zn	Per cent Fe	Per cent Co	Per cent As	Per cent Sb	Per cent Pb
A	Crude	25.32	0.82	0.19	3.10	.....	1.27	0.29	0.05
B	Single	22.34	None	None	0.002	0.016	None	None	
B	Double	14.93	0.008	None	Trace	None	None	None	
C	Single	20.80	Trace	0.001	0.007	0.053	None	None	None
C	Double	14.80	None	None	0.003	0.067	None	None	None

An example of nickel made in the electric furnace from refinery by-product salt showed 98.98 per cent nickel, 0.29 per cent copper and 0.73 per cent iron.

Antimony is marketed chiefly in "metallic" form as its principal use is in the manufacture of alloys. It should be sufficiently pure to show clearly marked "stars" on the surface of the pigs. It can also be marketed as a "hard" lead.

Bismuth is produced as metal in very pure form, usually obtained by electrolytic refining.

Arsenic is marketed as a 99 per cent arsenious oxide readily obtained by sublimation from many flue dusts.

Cobalt is marketed almost entirely as oxide. There are three oxides of cobalt and all have a market demand. They are difficult to prepare and the trade requirements are based on previous production rather than on any rational specificatiou. The great use of cobalt oxide is as an offset to yellow cast in clay and similar material, the powerful blue characteristic of cobalt salts being equivalent to a bleach.

Selenium is produced in granular or fused form, 99 per cent pure. The black variety, not too finely ground, is desired by the glass industry.

Tellurium is usually offered in an impure state but no market standards have as yet been developed.

Metallurgy.—The general treatment of the electrolyte for the recovery of a crude nickel sulphate has already been discussed in Chapter VI. This method also gave a cathode sludge of arsenic and copper from which a certain amount of arsenious oxide could be recovered if desirable. The balance of the impurities were either lost in blast furnace slags or concentrated in anode slimes.

TABLE 35.—ANALYSES OF ANODE SLIMES

Per cent	Raw			Boiled	
	A	B*	C	D	E
Copper	14.3	43.3	20.0	1.60	1.14
Silver	35.0	17.2	37.0	41.5	29.5
Gold	0.64	0.12	0.6	0.7	0.7
Platinum	.....	0.00017	....	0.0007	....
Palladium	.....	....	....	0.0006	....
Nickel	5.25	0.08	....	0.89	1.07
Cobalt	.....	0.006	....	....	....
Arsenic	2.68	3.03	4.0	1.42	1.20
Antimony	5.35	3.46	8.0	3.84	5.70
Bismuth	0.46	0.11	....	0.37	0.20
Sulphur	1.69	13.21	....	2.48	1.97
Iron	0.17	0.36	....	0.24	0.26
Lead	2.44	0.76	....	7.33	18.60
Selenium	5.70	1.20	....	12.94	11.24
Tellurium	2.69	2.10	....	5.72	6.20
Zinc	Trace	0.09	....	Trace	Trace
Silica	4.40	0.18	....	5.29	4.71

The analyses given in Table 35 are representative of such slimes. The wide variation in the composition is due to different conditions obtaining at different plants and this lack of a uniform product has been one of the difficulties in the way of a wet treatment of slimes. *A* is an ordinary slime with nothing unusual in the composition. *B* is produced by the electrolysis of converter anodes; its nature is reflected in the high copper and sulphur contents. *D* and *E* are analyses after the slime has been somewhat oxidized and leached with dilute sulphuric acid to remove the excess copper; they show noteworthy amounts of selenium present. The high lead content of *E* results from anodes carrying 0.2 per cent lead.

There is room for division of opinion as to the exact compounds present in anode slimes. The silver, gold, and a large part of the copper in slimes from well-refined anodes are doubtless in metallic or alloy form. Selenium and tellurium may be present in elemental form or as selenides, etc. Lead is probably as sulphate and much of the nickel, iron, cobalt, arsenic, antimony and bismuth in some oxidized form, but antimoniates and analogous compounds as well as simple oxides may easily be present. In general the slime is in an oxidized condition since the prior processes in the converter, the anode furnace and during electrolysis are all strongly oxidizing. The less noble metals are all therefore more or less oxidized in the slime when drawn from the electrolytic tanks.

There is always a high percentage of copper present. In slimes from converter anodes this is due in part to undecomposed matte, but even in slimes from the purest anodes there is a considerable amount of very finely divided metallic copper to be found after all cathode needles, etc., have been carefully screened out. This probably comes from either mechanical disintegration of the anode under electrolysis or from chemical oxidation of cuprous salts formed at the anode. Any one interested in the various possible explanations of this action would do well to consult an article by Dr. Emil Wohlwill on anode disintegration in the 1903 volume of Zeitschrift für Electrochemie.

Requirements for a Slimes Process.—Perhaps the foremost requirement for a metallurgical process for the treatment of these complex slimes is that there shall be a minimum of loss of the precious metals. We are dealing with material which usually runs 35 or 40 per cent silver and half a per cent of gold (and at times much more). This means that every by-product must be retreated for values contained. The second question relates to the interest on metal value. The slimes are worth about $5 a pound and a process is needed which will turn out the great bulk of the gold and silver promptly. A third desideratum is to be able to recover as by-products any marketable impurities which are present in commercial amounts. Then we have to consider the chemical questions introduced in the parent process of copper refining by the presence of any unusual reagents. Finally we have to reckon with the operating cost of the process in question.

This problem of treating anode slimes is doubtless the most difficult presented by the metallurgy of copper refining, and it is also the one which to-day leaves most room for further improvement. It has always afforded a field of contest for advocates of wet against advocates of fire processes; and the methods used at present employ a mixture of the two, the wet processes, however, steadily encroaching as time passes. We shall first discuss present practice and then the possible points of attack for further improvement.

The general problem as at present handled involves three main steps: first, the production of a nearly copper-free slime; second, smelting this to doré bullion; and third, parting the doré.

Slimes Boiling.—As sulphuric acid is a cheap reagent and as sulphate of copper is the basis of the electrolyte, the obvious method by which to remove the copper from the anode slime is to convert it into sulphate. As copper is not readily soluble in dilute sulphuric acid, however, either strong acid or some oxidizing agent such as air or nitre must be used.

The practice in the earlier plants was to screen the slimes through 60 or 70 mesh copper wire into agitators, using water to force the slimes through the screen. These agitators were lead-lined tanks about six feet in diameter and six feet deep, carrying a two-bladed paddle 2½ in. from the bottom and driven 12 rotations per minute. The blades tended to raise the slimes from the bottom. A charge consisted of perhaps 1000 lb. of slimes. After these were sluiced down into the tank liquor was siphoned off and enough sulphuric acid added to make a 50 per cent solution. A steam pipe heated the charge to the boiling point, the paddles were started and 100 lb. soda nitre added, a few pounds at a time. Owing to the strong evolution of poisonous nitrous fumes the nitre was added only at night and the treatment extended over two and sometimes three nights when the copper was found to be reduced to perhaps 3 per cent. The liquors made were sent to the electrolyte after carefully settling to free them from slimes.

After agitating, washing, and settling the charge, the supernatant liquor was siphoned off and the slimes, now running about 60 per cent moisture, dried to a thick mud carrying 25 per cent moisture by means of closed steam coils. This mud was considered ready for charging into the reverberatory refining furnace.

This method has been subject to many variations in details. At some plants compressed air is used for agitation instead of the paddles. Drying has been accomplished by the use of filter presses, of centrifugals or by direct heat instead of steam. It remained the general method, however, until the development of cyclical purification of the electrolyte which system made objectionable the introduction of large quantities of sodium salts into the electrolyte.

This difficulty was first met by charging raw slimes high in copper directly into the doré furnace. As will be later explained, such a procedure locks up a large quantity of silver in circulating by-products and is very undesirable.

The next step was the development of slimes-roasting and air has now come into general use as an oxidizing agent. In some cases an ordinary roasting hearth is used and in others patented[1] forms of tray hearths, but in any case all that is necessary is to expose a shallow layer of slimes to a low heat with sufficient air passing to hold the temperature below the fritting point (the slimes often ignite and overheat from the heat of oxidation), while being very careful not to stir the bed, and produce dust losses. The resulting calcines are then leached with dilute sulphuric acid which readily reacts with the cupric oxide formed in the roasting.

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[1] Wales, U. S. Patent.

A third process, which is patented,[1] mixes the filter-pressed slimes with concentrated sulphuric acid in sufficient quantity to satisfy the copper present, and heats this mud in a furnace the hearth of which is a steel basin. The slimes and acid are mixed first and pumped into the furnace. The mass is heated to about 450°F. with an oil burner and the mud occasionally stirred. The residues are practically dry and yield their copper sulphate readily when digested in hot water. This operation uses but a chemical equivalent of acid which is an advantage in some cases.

These various oxidizing and leaching processes designed to separate the copper from the rest of the slimes can be made to bring the residues down to 1 per cent or less in copper, with careful handling. The other elements present are also more or less affected by the operation. During the process more or less silver sulphate is formed, but this at once reacts with the copper present to form copper sulphate and metallic silver. In fact boiling is generally continued until the presence of silver in solution is shown by a salt test. When a decided precipitate is shown a small quantity of raw slimes is added to precipitate this silver and it is then certain that sufficient work has been done to oxidize practically all of the copper. In roasting the more volatile elements sublime to a certain extent and such flue dusts are a fruitful source of selenium, for example. Solutions from the boiling tanks always show nickel, arsenic and antimony extraction.

Smelting to Doré.—Whatever be the method employed in leaching the bulk of the copper from the slimes, the residue is always smelted to doré in some type of reverberatory furnace. Were the slimes subjected to a quiet fusion three layers of molten material would form with a distinct separation by specific gravity. At the bottom would be a foul doré bullion; in the middle would be what could be called a matte, silver being the principal metallic component and selenium substituting for the usual sulphur; then on top would be an arsenic-antimony slag.

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[1] Keller, U. S. Pat. No. 1110493.

It is quite possible to base a process on such a fusion of raw slimes with subsequent separation and special treatment for the three resultant products. However, we should get but about half of the silver and most of the gold in a bullion around 900 fine, while most of the balance of the silver would be tied up in the copper-silver-selenium-tellurium matte. This matte is a troublesome material to handle without making undue losses or tie-up of silver, and it is because the quantity made is more or less proportional to the amount of copper present that it is desirable to eliminate this last element as far as possible before smelting.

The earlier work was done in cupels with the addition of lead, the process being in a cycle of charging, melting, skimming, cupeling with a blast, skimming and pouring. Something like 10 per cent of the lead used in this process would be lost, and the resulting slag (Table 36) would have to be retreated on a lead basis and therefore was generally shipped elsewhere.

TABLE 36.—ANALYSIS OF LEAD CUPEL SLAG

	Gold	Silver	Copper	Lead	Iron	Silica
Skimming.......	0.0017	1.62	5.42	32.51	4.87	14.02

Then the use of lead was abandoned in favor of straight reverberatory smelting in small basic furnaces, air being forced under the surface of the bath to promote oxidation. It is interesting to note in passing that the silver furnaces of to-day are as large as the copper reverberatories in the earliest refineries. The general plan of operations is to melt the charge, thin the first slag with such fluxes as silica, soda ash, salt cake, etc., skim, blow the small quantity of matte to a second slag and bullion, skim, fine the doré with air and nitre, skim, and pour. Table 37 gives representative

Table 37.—Analyses of Doré Furnace Products

Per cent	Slimes	1st slag	2d slag	Doré	Flue dust
Copper	2.39	4.25	7.90	1.34	0.1
Silver	40.0	4.03	3.31	96.345	5.0
Gold	0.767	0.041	0.0041	2.37	0.017
Nickel	1.94	7.58	1.02	0.0065	
Arsenic	2.34	1.593	0.73	0.0075	2.65
Antimony	5.91	11.34	3.30	0.0084	10.9
Bismuth	0.343	0.5378	0.64	Trace	
Sulphur	2.80	0.264	0.90		
Iron	0.23	5.63	3.88	0.1233	
Lead	5.43	6.14	2.78		
Selenium	11.89	1.58	11.06	0.0020	35
Tellurium	5.45	1.80	19.36	0.0068	1.5
Zinc	Trace	Trace	Trace	None	
Silica	4.25	19.90	2.26		
Alumina	......	4.93	2.15		
Magnesia	......	1.604	1.31		
Lime	......	1.075	0.18		

analyses of the various metallurgical products produced by such a procedure. While the several columns are not all strictly comparable, they are near enough so to give a good idea of the character of the products. Had not the matte made been charged back or broken down before skimming we should have had another product running about 26 per cent silver and 0.02 per cent gold.

It is interesting to note the relative concentrations of the various elementsin the different products—the slimes produce roughly 25 to 30 per cent first slag, 15 per cent second slag, 30 per cent doré, and 20 per cent flue dust, plus volatile losses and minus fluxes and furnace material. Perhaps the most striking thing is the "spreading" of the silver-gold ratio, nearly all the gold going directly into the doré while the silver spreads over the various by-products. This ratio as the figures stand is as follows: Slimes, 52.2; first slag, 98.4; second slag, 806; doré, 40.6; flue dust, 293.

The gold content of the slags is quite satisfactory metallurgically, but the silver is entirely too high. When the slag is reasonably fusible, it is possible by desilverization, consisting of a melting and collection of the suspended values, to bring the silver down to 0.5 per cent, but as these slags are all retreated in the anode furnace this seldom pays.

The elements which do not readily form fusible slags and therefore float undigested on the surface of the bath and those (such as lead, iron, and antimony) which on the contrary form slags very readily, tend to concentrate in the first slag. It is such an impure and unpromising material that it does not offer much chance for the recovery of by-products. Were the nickel out of the way it could be reduced to an impure antimonial lead.

The second, or soda slag really represents impurities subsequently blown out of the base bullion and matte formed when the slimes were melted. Here we have a decided concentration of tellurium, an element which clings tenaciously to silver. Since sodium salts are generally soluble, over half the total contents of this slag can be leached out with hot water. This is the starting point for the recovery of tellurium.

The small quantity of nitre slag made when fining the doré is charged back into the furnace with the next lot of slimes.

The flue dust shows a remarkable concentration of selenium and it is from this source that the market demand is supplied. Elemental selenium may be readily prepared from this dust in several ways—by fractional sublimation, by leaching followed by electrolytic precipitation, or by leaching followed by chemical reduction. The last-named method is perhaps the most satisfactory. The leaching is generally conducted in the presence of hydrochloric acid and a strong oxidizing agent such as a chlorate and preferably exposed to sunlight. The resulting solution is strengthened in free hydrochloric acid in order to hold back the tellurium, and the selenium is then precipitated as a red powder by sulphur dioxide gas. This powder is melted and skimmed to a bright face, when it is cast into cakes as the black variety. If desired, the powder can be dried in an oven, the heat changing it to the black variety and the baked product then ground for the market. Selenium often runs 99.5 per cent Se and the chief impurities are lead sulphate, arsenic, antimony and tellurium. The lead content is the most difficult to control.

Parting the Doré.—We have too well recognized methods available by which to part gold and silver—the sulphuric acid and the electrolytic. Both are in use and each has its advocates but the latter has come into more general use chiefly on account of its greater cleanliness.

In the acid method, the doré is cast into slabs resembling waffles, the indentations giving additional surface for corrosion. The process is very simple, being the production of silver sulphate by the decomposition of strong, boiling, sulphuric acid by silver, sulphur dioxide being given off. The gold is left undissolved and is melted in a crucible, while the silver sulphate, which is readily soluble in excess of free acid, is precipitated upon copper sheets to form sponge silver which is washed and melted. The copper sulphate solution is sent to the copper-refining tanks.

The plant required is inexpensive—needing only a couple of cast-iron pots, a lead-lined tank and a crucible furnace—and the tie-up of values is short, being about 48 hours. On the other hand the process is dirty; hot sulphuric acid is hard to handle; and the fine silver cannot be brought below a third of an ounce in gold. Also, if the doré is high in gold, the acid attacks it slowly and it is necessary to inquart it.

The hot liquor from the kettles runs about 600 grams per litre silver and twice as much free acid. This has to be diluted with water before the silver is precipitated, and the tank house must be able to absorb this free acid. The kettles are fired up and boiled until no solid pieces of doré can be felt with a stirring rod. This takes about eight hours. The liquor is drawn off to a heated settling kettle to free it from entrained gold, fresh acid is added, and then given an additional boil to free the gold of silver. By washing the gold precipitate thoroughly before adding this acid it is possible to make 995 gold sand directly in the kettle. The silver sponge should run 998 or better.

The electrolytic process consists of the electrolysis of doré anodes in a copper-silver nitrate electrolyte. Three methods have been employed—the Thum-Balbach, the Moebius and the Whitehead. The first method uses horizontal carbon cathodes laid as the floor of a shallow earthenware tank, the anodes being carried in a basket within a light cotton bag to collect the gold slimes. At an efficiency of 90 per cent, 3.5 volts per cell is equivalent to a recovery of about 32 oz. silver per kilowatt-hour. The current density is limited to about 35 amperes per square foot by the heating of the electrolyte, as a hot solution means a high loss of free nitric acid. The silver crystals have to be frequently removed in order to prevent treeing, which will reach and puncture the gold bag.

The electrolyte consists of about 4 per cent copper as nitrate, 2 per cent silver as nitrate, and 0.1 per cent free nitric acid. Copper enters from the doré and silver dissolves in a certain excess, nitric acid being regularly added, but the entrained liquor in the silver sponge removed holds the balance steady. The wash waters from this sponge are not returned to the parting tanks. There is no circulation of the electrolyte and each cell is a complete unit.

The silver crystals are readily washed with water and if the copper in the electrolyte is low, silver very close to 1000 fine can be produced. As this is not desired, however, the copper is allowed to build up to a maximum of perhaps 6 per cent in the electrolyte before any deliberate removals are made.

There is no anode scrap as the remnants of anodes are left in place on the horizontal trays until they are entirely consumed. Cathode silver runs 0.1 oz. per ton in gold or even better.

The gold mud is periodically removed and boiled in strong sulphuric and in nitric acids to remove the silver.

This mud is also the raw material for the recovery of platinum and palladium, as mentioned later.

The Moebius process substitutes a vertical system of electrodes which is very much more compact and yields more silver per kilowatt-hour, due to lower tank resistance. The silver crystals drop to the bottom of the tank, in some plants being knocked from the cathode by a simple system of swinging wooden rakes. The anodes are inclosed in sacks. Against the cheaper first cost and somewhat lower power required, there is more care required to prevent gold leaks, the cell is not so open to constant inspection, and there is a small amount of anode scrap made.

The third system, which I have called the Whitehead plan, has not come into general use, although it has been more or less extensively employed at some of the government plants. It uses gelatin to obtain a coherent deposit to be stripped from silver cathodes and duplicates in many ways the conditions found in a copper refining cell.

As compared with the sulphuric acid method of parting, the products are more pure, there is less danger of metal loss, in a large plant the operating costs are somewhat lower, and but little by-product liquor is made. On the other hand the first cost of plant is much greater, in a small operation the operating costs are no lower, while the metal tie-up is at least 50 per cent more.

If platinum and palladium are present in the doré we have the choice between electrolytic and chemical recovery. If the gold slimes from the parting are boiled to dissolve their silver in sulphuric acid, these metals remain with the gold which can then be electrolyzed by the Wohlwill process in a chloride electrolyte; if nitric acid is used in the gold boiling, the platinum and palladium go chiefly into solution and after a somewhat tedious treatment may be recovered as double chlorides with ammonium. The platinum is thrown out singly by sal ammoniac from a reduced solution; after oxidation the palladium may be similarly precipitated. Metallic sponges are obtained upon ignition of these precipitates. As these sponges are difficult to melt the metal is usually marketed as a crude powder. The separation between the two metals is quite sharp and a product 98 per cent or better is readily obtained.

The Wohlwill process has two great objections: it ties up a very valuable metal, and it exposes it to possible theft. In ordinary practice the gold does not appear in solid yellow metal until it is almost ready to ship. Crude, dirty products are hard to sell and do not present the same temptation to laborers handling them. On the other hand the electrolytic process is cleaner, as in the case of silver parting, with the result that most government plants use electrolytic and most private plants chemical extraction. As before stated, the government does not pay for platinum contents of deposits; one reason for this is that the assay method for accurate results is very tedious and expensive and its application would result in great delays in making settlements.

Slimes Process Development.—The progress already made with the metallurgical problems presented by copper anode slimes may be seen from Figs. 25 and 26 which are flow sheets representing practice twenty years ago and today. We may now consider the various points at which the second process may be attacked.

Screens.—The fact that a certain part of the copper carried in the slimes may be removed by simple screening suggests the possibility of further separation by mechanical means:

The first point of attack here is against the size of the particle—could the slimes be classified in any way by screening? The practice at one plant is to screen out nodules and large pieces by passing the slimes through a 4-mesh screen, and then through a 70-mesh screen, which takes out float slime such as was discussed in Table 24 in the last chapter. Changing the size of this fine screen and then analyzing the slimes gave the results shown in Table 38, below, which indicate the hopelessness of such a classification.

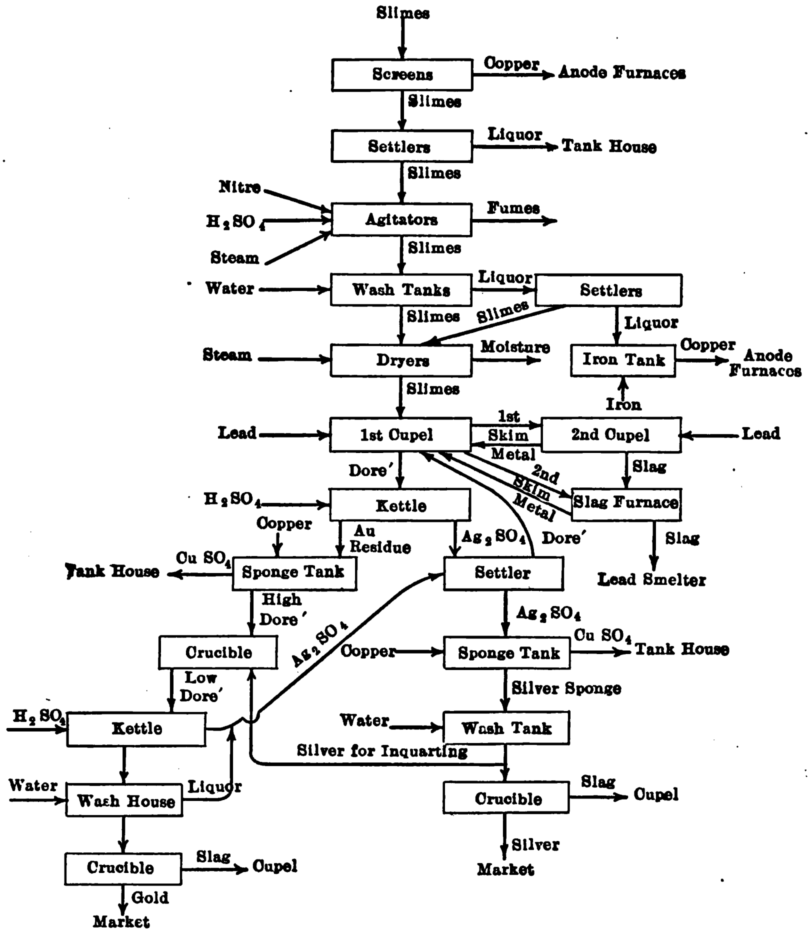
Slimes
Screens
Copper
Anode Furnaces
Slimes
Settlers
Liquor
Tank House
Slimes
Nitre
H_2SO_4
Steam
Agitators
Fumes
Slimes
Water
Wash Tanks
Liquor
Settlers
Slimes
Slimes
Liquor
Steam
Dryers
Moisture
Iron Tank
Copper
Anode Furnaces
Slimes
Iron
Lead
1st Cupel
1st Skim
Metal
2nd Cupel
Lead
2nd Skim Metal
Slag
Dore'
Slag Furnace
H_2SO_4
Kettle
Copper
Au Residue
Ag_2SO_4
Dore'
Slag
Lead Smelter
Cu SO_4
Tank House
Sponge Tank
Settler
High Dore'
Ag_2SO_4
Ag_2SO_4
Crucible
Copper
Sponge Tank
Cu SO_4
Tank House
Low Dore'
Silver Sponge
H_2SO_4
Kettle
Water
Wash Tank
Silver for Inquarting
Water
Wash House
Liquor
Crucible
Slag
Cupel
Crucible
Slag
Cupel
Silver
Market
Gold
Market

FIG. 25.—Slimes process—1900.

TABLE 38.—ANALYSES OF SLIME THROUGH DIFFERENT SIZE SCREENS

Meshes per inch	Per cent copper	Per cent arsenic	Per cent antimony
– 4	21.3	6.00	2.44
– 80	19.6	5.39	3.10
–120	19.4	5.50	3.92
–200	21.3	4.30	3.60

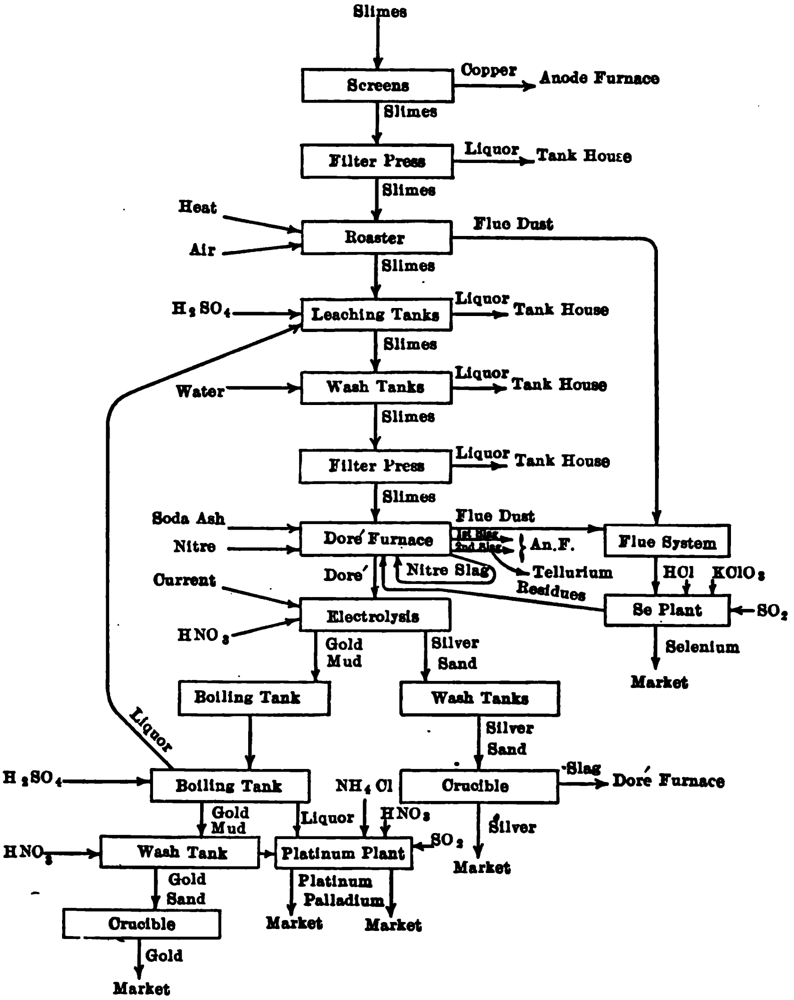
Slimes
Screens
Copper
Anode Furnace
Slimes
Filter Press
Liquor
Tank House
Slimes
Heat
Air
Roaster
Flue Dust
Slimes
H_2SO_4
Leaching Tanks
Liquor
Tank House
Slimes
Water
Wash Tanks
Liquor
Tank House
Slimes
Filter Press
Liquor
Tank House
Slimes
Soda Ash
Nitre
Doré Furnace
Flue Dust
1st Slag
2nd Slag
An.F.
Flue System
Current
Doré
Nitre Slag
Tellurium Residues
HCl
$KClO_3$
Se Plant
SO_2
HNO_3
Electrolysis
Gold Mud
Silver Sand
Selenium
Market
Boiling Tank
Wash Tanks
Liquor
Silver Sand
H_2SO_4
Boiling Tank
NH_4Cl
Crucible
Slag
Doré Furnace
Gold Mud
Liquor
HNO_3
Silver
HNO_3
Wash Tank
Platinum Plant
SO_2
Market
Gold Sand
Platinum
Palladium
Crucible
Market
Market
Gold
Market

FIG. 26.—Slimes process—1915.

A screen analysis of slimes is given in Table 39. Here we happen to have a sample which has some small cathode debris present and the effect of screening this out is at once apparent upon the copper assays and the use of one fine screen is justified. In Table 38 the assay is for the total slimes passed by the screen while Table 39 gives results for a true screen analysis. A 70-mesh screen will ordinarily retain 8 or 9 per cent of the weight of slimes sent it from the 4-mesh, and this quantity may be advantageously returned to the anode furnace.

TABLE 39.—SCREEN ANALYSIS OF SLIMES

Mesh passed	Mesh retained	Grams	Per cent weight	Per cent copper	Grams copper	Per cent total copper
4	20	319.1	55.6	40.8	130.2	74.3
20	40	101.4	17.6	27.0	27.4	15.6
40	60	54.0	9.4	22.0	11.9	6.8
60	80	30.8	5.4	13.7	4.2	2.4
80	100	14.4	2.5	10.6	1.5	0.9
100	...	54.3	9.5	Not run		
Total.....	...	574.0	100.0	30.6	175.2	100.0

As the silver and gold are presumably present in metallic form and as they have a higher specific gravity than most of the other elements present, some gravity separation might classify the product. Careful trials with a Wilfley table did not effect sufficient separation, however, to enable any process to be built on such a basis. It is just possible that the application of recent flotation experience might show something of value. It must be remembered that what is necessary is not so much a perfect separation —any process will have to work up its intermediate products for precious metal values—as a scheme whereby the great bulk of the silver and gold will be put on the market promptly, leaving the more tedious working of other by-products until the last. One of the objections to present practice is that the other elements are gradually removed until the pure silver and gold are obtained, thereby holding the entire value until the very end of a long process.

Oxidizing the Copper.—The next step in the present process is oxidation of the copper. It has already been pointed out that the presence of any quantity of copper in the doré-furnace charge makes a serious amount of by-product matte high in silver. If the copper is allowed to stand at 15 or 20 per cent and the slimes charged directly into the furnace, instead of obtaining 30 per cent first slag, 15 per cent second slag and 30 per cent doré we should get perhaps 35 per cent slag, 25 per cent matte and only 20 per cent doré, a third of the silver being tied up in the matte. The desirability of the awkward oxidation step is thus fully demonstrated.

In the endeavor to simplify this operation, considerable work has been done experimentally with ferric sulphate as an oxygen carrier using the well known reactions:

$$Cu + Fe_2(SO_4)_3 = CuSO_4 + 2FeSO_4$$

and

$$2FeSO_4 + CuSO_4 + \text{current} = Fe_2(SO_4)_3 + Cu.$$

A diaphragm cell is all that is necessary to carry out this process and chemically it is very pretty. The fact that it has not been successfully applied even in the hands of those skilled in electrolysis bears witness to the great difficulties interposed by a diaphragm cell in an acid process. Later work such as that of Hybinette in nickel or the use of a chemical retarder[1] may reopen this field.

Leaching.—The next step of dissolving the oxidized copper from the slimes is true leaching, and leads to the consideration of the possibility of dissolving the bulk of the slimes at once instead of making this a mere preparatory step to furnacing.

The first suggestive point to be noted is that in any of the oxidation processes it is easy to carry the action to a point where large quantities of silver may be taken into dilute sulphuric acid solution as sulphate. It is further known that by careful temperature regulation, a very high grade selenium product may be obtained in the flue. On the other hand, anything but an incipient roast tends to frit the easily melted slimes, spoiling the physical condition for subsequent leaching and forming undesirable chemical compounds of copper, arsenic, etc. Roasting therefore offers possibilities which are limited by difficulties in practical operation.

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[1] Addicks, U. S. patent No. 1138921.

A second method of attack is to digest the raw slimes in boiling strong sulphuric acid. This readily dissolves nearly the entire content and yields a very foul solution of sulphates and an impure gold residue. Fortunately silver forms one of the very few insoluble chlorides and the plan would be to precipitate the silver with salt and reduce the chloride to metallic silver.

We have now a plan which would promptly yield the bulk of both the silver and the gold for marketing while leaving the less valuable constituents behind for working up into various other by-products. Such a plan may yet develop commercially but there are again some serious practical problems to be overcome. In the first place a certain amount of flour gold is formed and it is very difficult to keep this away from the silver chloride precipitate. If the latter is not free from gold it has to be parted, incurring corresponding delay and expense. Silver sulphate is not a readily soluble salt and a considerable bulk of valuable liquor has to be handled. The reduction of silver chloride can be done electrolytically or chemically but even that is not complete and the question of small quantities of chloride being volatilized during melting has to be considered.

On the gold side we have a sludge carrying lead and antimony as well as the gold, and this involves fluxes and slags in the refining.

The other elements are collected in a bulky, dilute solution carrying sulphates and chlorides and any simple separation is a chemical problem of no mean order.

Smelting.—Another possibility lies in directly melting the raw slimes in a furnace with separation of slag and matte leaving most of the gold and half to two-thirds of the silver in a doré bullion which can be quickly fined and parted. The slag can be returned to the anode furnace as at present and the matte subjected to some special process.

The direct blowing of this matte in a small Bessemer converter is the most obvious method. We would get a selenious oxide fume and a copper-silver blister as the products, which would be quite satisfactory metallurgically.

The difficulty lies in the lack of courage to face the possible silver losses. Now that the Cottrell process has been so successfully applied to silver flue losses[1] this might be reconsidered.

Another method is to pulverize this matte and leach the values, pre-roasting if desired. This really means leaching out the copper and we have simply rearranged the steps in the original process so as to more promptly release part of the values.

Smelting has the advantage that a fair separation of other impurities is made in concentrated form, easily stored for retreatment.

Parting.—This step is in a very satisfactory state of development and but little improvement in methods is to be looked for.

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[1] Aldrich, Transactions American Electrochemical Society, Vol. xxviii, p. 119.

CHAPTER VIII

FURNACE REFINING

In the early days copper was produced by a succession of roasting and fusing operations based upon the fact that copper sulphide when melted with copper oxides reacts to form sulphur dioxide gas and metallic copper. This was the basis of the celebrated Welsh process. Then it was found that if the operation was so conducted that a small metal fall was obtained first, these "bottoms" would contain most of the impurities, including gold (silver was frequently separated by a sulphatizing roast and subsequent wet extraction), and the balance of the copper produced would be correspondingly purer. This is the characteristic "best selected" process used in England and the basis of the "Argo" process for separating gold from copper.

While converting has supplanted roasting and electrolysis reverberatory refining for the great bulk of the world's copper, although the melting of Lake mineral in Michigan and various small-scale operations abroad are notable exceptions, the electrolytic process has retained two reverberatory steps, the anode and refining furnace operations, in the metallurgical scheme.

Blister copper produced directly by the converter does not make desirable anodes, although special conditions have at times made their use profitable.[1] For the general case the principle has been well established that work which can be done in the anode furnace should not be done in the tank-house. The guiding principle in tank-house operation is to do whatever is necessary to obtain uniformity of operating conditions, and converter anodes give trouble unless a very pure blister is being treated.

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[1] Burns, *Trans.* A. I. M. E., vol. xlvi, p. 711.

The function of the anode furnace is to make a perfect anode casting in which the sulphur has been thoroughly removed and other oxidizable impurities slagged off as far as possible.

The refining furnace serves merely to put the cathodes into desired physical shape and beyond the elimination of traces of sulphur and adjustment of "pitch" has ordinarily no chemical function. Nevertheless the methods of operation of the two furnaces are identical in many respects and the discussion of the general principles involved is applicable equally to both.

Just as many of the operations in smelting are based upon the marked affinity between copper and sulphur, so the basis of furnace refining is the relative weakness of the affinity between copper and oxygen. The general plan is therefore to oxidize the impurities the oxides of which will then either escape by sublimation or float on the surface of the bath, from which they may be skimmed or slagged. According to this method it should be possible to remove all elements less noble than copper, leaving simply silver, gold and the platinum group alloyed with the copper. The same principle of resistance to oxidation is reversed in the tank house, the copper oxidizing to sulphate at the anode and the more noble metals remaining behind in the slimes. Theoretically we have, therefore, a perfect separation of the copper, the impurities and the values.

In practice the system does not work out so perfectly, as mass action comes into play. It is quite easy to remove the bulk of most oxidizable impurities in the anode furnace, but as the amount present becomes less and less it is increasingly difficult to make further removals, and carried to absurdity the entire charge would be slagged in order to remove the last traces. Then some elements such as arsenic readily form direct compounds with the more basic metals, and these cannot readily be broken up. The degree of elimination of impurities depends therefore upon: (1) the amount of impurity present; (2) its affinity for oxygen; (3) its affinity for copper, and (4) the extent to which scorification is pushed.

Scorification consists of using an element as an oxygen carrier. In this case the principal scorifying agent is copper in the form of cuprous oxide. The process is to oxidize with an air blast some of the impurities directly and a part of the copper by air. The cuprous oxide formed dissolves in the bath and penetrates to all parts of it, reacting with elements which have a greater affinity than copper for oxygen and reducing out an equivalent amount of copper. These basic oxides further react with any acid material, such as silica in the furnace walls, that may be present and the resulting slag is skimmed off, leaving a purified bath holding a considerable quantity of cuprous oxide in solution.

The reducing stage necessary to throw back the cuprous oxide is now accomplished by generating a hydrocarbon gas by the destructive distillation of hard wood poles thrust beneath the surface of the bath, which is covered by a blanket of carbonaceous material to protect it from any further oxidation. The various steps will now be taken up in detail in the order in which they occur.

Charging.—A reverberatory furnace is used for this work operated on a twenty-four-hour cycle. Starting with an empty furnace the first operation is charging. In the early days this was accomplished by hand, one pig or cathode being charged at a time. Two men would lift a pig to the end of a peel held in position at a charging door by a third man. This peel was a long heavy steel bar flattened like a paddle at one end. The three men would then thrust the peel into the furnace and flip the pig off at the desired location.

Various mechanical devices were tried to improve this practice, but for a long time the only successful innovation was the use of air lifts and tongs in placing the pigs on the peel. As furnaces gradually increased in size the time required to charge them became inordinate, and not only was the twenty-four-hour cycle badly disarranged, but the furnace cooled off badly during the delay. These difficulties led to trials of charging cranes developed in the open-hearth steel industry, but they were at first unsuccessful, due to a lack of appreciation of fundamental differences between the two problems. The open-hearth furnace has a small charge simply thrown in it while the copper reverberatory by the old practice was piled with pigs clear to the roof. The first result of mechanical charging was an enormous loss in cold capacity which more than offset the other advantages gained. This failure checked further development along these lines for some time until a special form of peel consisting of a fork with a special pushing device[1] was devised to replace the upsetting shovel of the old type. This crane met with immediate success, and it was found possible to charge 5000 lb. at a time at a rate of at least 200,000 lb. an hour and lose nothing in cold capacity as compared with the hand method, while at the same time charging a 200-ton furnace as quickly as the old 50 and 75-ton units had formerly been handled.

The main thing in charging is to have material which will stack well. This means that pigs should have a good blister finish and not be overblown and that cathodes should be reasonably smooth. When this is not the case individual charges after piling in the furnace will spill and take up much more space.

The next development along this line was the use of the crane for recharging after melting the first batch. In this way a certain molten tonnage in excess of the normal cold capacity of the furnace can be obtained.

Then it was found that anode scrap could be recharged to a certain extent while the metal was being poured. Finally cathodes were successfully charged while the copper was being poured.[2] This will be referred to again later on.

In this way the limit to size has been practically eliminated as mechanical charging will rapidly take care of any size of furnace which can be built and the cost has been brought down greatly as the hand method exposed the crew to very severe heat.

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[1] Prosser and Ladd, U. S. Patent.

[2] Addicks and Marks, U. S. Patent No. 980584.

Melting.—The next step in refining is the melting of the charge. This consists merely of burning as much fuel as the furnace can take care of. Copper is a good conductor of heat and the piled-up charge through which the hot gases have to filter absorb heat very rapidly. The melting is divided into three stages: (1) "softening," when the hot mass collapses; (2) "coming flat," when the molten metal covers the softened mass; and (3) "coming afloat," when the balance remaining on the bottom is absorbed.

It has been found that a semi-bituminous coal running about 20 per cent in volatile matter gives a desirable length of flame for this work. It is most essential that the coal should not form a fusible ash as deep fires are carried, and unless they are free burning a great deal of delay is encountered. In a refining furnace the old practice has been to fire heavily during the early stages of the refining and carry a bed of coke for heat during the later part so as to avoid sulphur from the fuel reaching the copper. With the present large charges, and particularly when recharging, while pouring it has been found necessary to fire more steadily and without any apparent untoward effect.

Flapping.—When the charge is afloat a button is taken in a "say ladle," and if this throws a "worm," indicative of sulphur, a pole is introduced to agitate the bath, which is exposed to the air until a button sample shows a surface which is unbroken on cooling. This practice has a bearing on "overpoled" charges of refined copper to be taken up later.

The system of using buttons for samples is very old, but still stands as the best method of controlling furnace refining. A small ladle with a cup about an inch and a half in diameter is warmed by holding over the bath for a moment, then used as a rabble to sweep a clean face at the spot where the sample is to be taken and then plunged beneath the surface and quickly withdrawn. The sample thus obtained is allowed to "set," when it may be dumped into water to cool for handling. Both the surface and the fracture upon nicking with a chisel and breaking in a vise give clear indications as to the state of the bath of copper. When sulphur is present a small volcano forms on cooling, which throws out a part of the metal which twists around as it chills much like a worm. When excess oxygen is present the surface shows a deep depression, and when the bath is nearly saturated with cuprous oxide this depression will break inward into a cavity. Copper at desired "pitch" for pouring will show a full rounding slightly wrinkled surface. Overpoled copper begins to "spew" and show the above-mentioned sulphur indications.

In the same way the condition of affairs may be noted by the color and structure of the fracture. When copper is saturated with cuprous oxide (about 6 per cent Cu_2O, beyond which point further oxidation will only cause useless slagging) the fracture shows a marked cubical structure, brick-red in color. As the oxygen is poled out the structure becomes more fibrous and the color brighter until we reach the lustrous silky texture corresponding to properly refined copper.

These simple tests enable a practiced eye to follow the refining operations with very satisfactory accuracy, and consequently metallographic and other methods have not come into use to any extent.

When the sulphur has been poled out the flapping or blowing begins. Originally a rabble was swung from a chain at the furnace door and the surface of the metal flapped or broken into spray by swinging this back and forth with free admission of air at all doors. This is hot and fatiguing work, and as the size of furnace charges increased it again became necessary to find some mechanical substitute. This was accomplished by blowing compressed air beneath the surface of the bath, sending up a fountain of molten metal instead of a mere splash and at the same time thoroughly stirring the bath itself. The great objection to this procedure has from the beginning been the consequent damage to the furnace structure. The fountain is so violent that more or less of the spray reaches the roof of the furnace and the metal highly charged with cuprous oxide avidly attacks the silica brick wherever it touches it. The large modern furnaces tend toward excessive repair costs as one of their disadvantages, and this corrosive action aggravates a situation already bad. When basic or neutral material such as chrome brick is substituted for acid brick construction, this trouble disappears; otherwise constant attention must be given to restraining the men in control of the air blast who naturally tend to over-vigorous application in order to gain time. Another remedy would be the use of low pressure air, which would not give such violent agitation, but the standard 80 lb. per square inch general service air system around the plant is generally utilized.

Chemically the method is very efficacious and the largest bath can be thoroughly saturated with cuprous oxide in a couple of hours at small expense. The iron pipe used gradually dissolves, but the amount of iron thus absorbed by the copper is proportionately so small as to be of no consequence even in a cathode melting furnace.

Skimming.—The next operation is the removal of the slag, which is simply pulled off with a rabble through the skimming door into suitable pots. The skulls are later broken up and if the slag made was reasonably fluid, the large amount of metallics always present can be easily sorted out and returned to the furnace. Often slag rich in metallics is returned to the next charge.

The general question of slag formation requires consideration at length and will be taken up later on.

Coking.—When the bath has been skimmed to a clean face, charcoal, coke or anthracite coal is spread over the surface to protect it from oxidizing influences during the subsequent poling operation. At first charcoal was exclusively used, particularly when melting cathodes, on account of its low ash and freedom from sulphur. Then the much cheaper low-sulphur coke crushed to suitable size was substituted, reserving charcoal merely for the covering on the pouring ladle between the furnace and the casting machine, where the finishing touches are always put in adjusting the oxygen content of the product. Finally buckwheat coal has been largely used on anode charges as the cheapest form of carbon for such work.

As this blanket of floating fuel burns away it has to be renewed so that no bare surface be exposed to possible oxidation.

Poling.—As regards poling, as the reduction of the excess cuprous oxide is called, little or no change has been made from early practice. As the furnaces have increased in size larger and longer poles have been used, but the method of forcing one end of a pole below the surface of the bath by using a chain tackle making an inverted lever against an iron cross bar is still in use. As the pole is consumed it is gradually fed in and a new grip taken with the chain until the stick becomes too short, when it is thrown into the furnace as a floating brand. Green hard wood gives the best results.

The poling operation is a very clumsy one. The poles are hard to handle and bulky to store. When a single charge takes twenty-five young trees to pole it up it may readily be seen that the surrounding country will soon be stripped of suitable timber and that transportation charges make poling cost an ever-increasing burden.

Oil poling has been tried with but partially satisfactory results. The reduction is very rapid when fuel oil is blown beneath the surface of molten copper, a few minutes' time corresponding to two hours' ordinary poling. In fact, its very rapidity of action is one of the objections to its use, as it is difficult to arrest the reducing action before the copper is "overpoled." Another serious difficulty attendant on the use of oil when poling cathode charges is that the copper absorbs sulphur or other impurities from the oil, which give a very curious appearance to its surface on cooling, and would doubtless make its sale difficult even if no objectionable property were imparted to it.

Finally oil poling is very variable in its expense. Apparently it is very easy to use twice the amount to pole one charge that is necessary for another, the excess oil being burned above the surface of the charge.

These difficulties have prevented the general use of direct oil poling. Nevertheless it seems probable that the time will come when gas poling will be used. It is evident that an outside source of heat can be used for the destructive distillation of wood or that oil or coal gas could be made suitable for the purpose. In the case of wood the cheapest available form of waste could be utilized instead of valuable young trees. Such a gas could be readily controlled in its action and a gas made from wood waste would require no purification.

As the poling operation proceeds sample buttons are frequently taken for examination, and when the desired amount of reduction as shown by these tests is nearly attained an ingot is poured and the nature of the "set" surface on the top of this casting inspected. When a full rounding surface is obtained the charge is ready to pour. Castings of different sizes require a different amount of unreduced oxide in order to obtain a level surface in an open mold. The final adjustment is therefore made in the casting ladle, where charcoal is added or allowed to burn thin according to the appearance of the set on the castings being made.

Should poling inadvertently be allowed to continue too long the charge becomes "overpoled," a condition the symptoms of which are much better understood than the underlying causes. The surface of a casting made from such copper swells as it cools until it breaks or "spews," giving a "worm" similar to that noted in connection with sulphur-bearing anode charges. While such a condition can be apparently rectified by a slight oxidation of the charge, copper in this state becomes unmanageable as regards its set, and such rapid vacillations are encountered while pouring that accepted practice is to flap the charge down again to "dry" copper and pole back to the proper oxygen content, or, in short, to re-refine the entire charge. The unstable condition can be controlled by adding certain substances, notably lead, in small quantities, but as mere traces of lead make copper brittle the cure is worse than the disease. It is probable that sulphur plays some part in this peculiar behavior.[1]

Pouring.—Furnaces up to 20 tons in capacity used to be ladled by hand, a group of five or six men each with a ladle holding some 15 or 20 lb. of copper forming an endless chain between the "ladle hole" and the molds. The latter were made of cast iron or copper placed over a shallow bosh and the castings were dumped by hand into the water from which they were fished with suitable tongs. The next development was the "bull ladle," which is still in use at some places. This was simply a large ladle slung from an overhead crawl, enabling one man to dip out as much at a time as the five or six had done before.

Then came the casting machines, which have developed along several lines. Three general types are in use—the endless chain conveyor first developed by McCoy, the well-known Walker wheel and the variation of this known as the Clark machine. These are all covered by various patents, most of which, however, have now expired.

The first, which has now gone out of use for wire bars, but is still occasionally employed for anodes and more recently in casting blister copper into pig, carried the molds on a link belt mechanism in front of the spout, then lowered them on inclined rails into a bosh of water and then dumped the castings as the molds returned upside down on the return trip underneath the bosh. The Walker wheel, as its name implies, has a central hub carrying the rotating mechanism and radial arms supporting the molds. The Clark machine differs from the Walker chiefly in that the molds are carried parallel to the radial arms while on the latter they are placed circumferentially, and still further modifications have been made at the new Great Falls plant.

The Walker scheme has two advantages over each of the other types due to the way the molds are placed when casting wire bars. When the length of the mold is in line with the stream of copper there is a decided wash, which tends to make "splashes" and "cold sets" in the finished bar. Then in order to bring successive molds in line it is necessary to start and stop the machine, which jars the partially set castings just made and tends to make "edges," while the Walker wheel runs continuously, the pouring being done on the fly, so to speak. The lost motion and jarring of the link-belt type of machine was the chief reason for its abandonment in addition to higher maintenance costs. The Clark machine has the advantage that it will accommodate the giant wire bars supplied to a certain extent to foreign wire mills.

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[1] Skowronski, *Trans.* A. I. M. E., vol. lx, p. 307.

As the size of furnace began to outstrip even mechanical means for casting, always having in mind the desirability of completing a furnace cycle in an even twenty-four hours, the multiple-lip ladle was devised. In this way as many as four wire bars or eighteen ingots are poured at one movement of the intercepting ladle. Then came the twin ladle, and it was demonstrated that casting could be conducted at the rate of over 100,000 lb. an hour. This could again be doubled by using two wheels.

The bars are carefully inspected before shipment and any minor defects such as small "fins" cut off with a hammer and chisel. The temperature of the bosh water and also of the molds has much to do with the appearance of the finished product, although color due to slight films of oxide has not the importance attached to it to-day that was formerly the case. The bars should be dropped into the water as soon as possible after solidification is complete. The molds, which upset but do not enter the water and are sprayed to cool them, should retain a temperature just sufficient to enable them thoroughly to dry and properly take the bone ash wash which is applied to prevent the bars from sticking. On the other hand, the temperature of the bosh water itself must be held down by a circulating system to a point where it does not interfere with clear vision due to clouds of steam given off.

Various materials have been tried out as substitutes for the rather expensive bone ash used in painting molds. It is necessary that the substance used should have a high melting point, have no tendency to enter into chemical combination with molten copper, and particularly give off no gaseous constituent under heat which would tend to make the casting porous.

Lampblack serves the purpose, but is not readily applied. A smoked mold gives a beautiful casting. Pulverized silica is another substitute, but as the finish given is not entirely satisfactory its use is confined to anode work.

Bone ash should be thoroughly calcined to be free from grease, which evolves gases in the mold. A typical analysis of bone ash is:

$Ca_3P_2O_8$	97.69 per cent
SiO_2	1.01 per cent
MgO	1.02 per cent
Total	99.72 per cent

Many of the minor physical defects in refined copper can be traced to improper mold wash.

Another matter which needs attention is the chemical composition of the water used for cooling the copper. It is quite possible by constant evaporation coupled with an impure make-up water to obtain concentrations of sodium chloride and other salts which will crystallize out on the surface of the hot molds in sufficient quantity to cause pinholes in the bars.

The molds themselves can be made of either iron or copper, but the latter gives the best results. For many years molds were made by filling a built-up iron box with molten copper into which was thrust a core imprinting the desired shape. This method involves a complicated calculation of shrinkages starting with an iron mother core to produce a copper mother mold, which in turn makes copper cores from which the final molds are obtained. To-day this has been largely superseded by molding in sand with an ordinary wooden pattern.

A mold generally fails by burning or by warping. Spongy spots can be hammered up, but a mold should be discarded before any appreciable sponginess is found in the castings produced. Cracks in a mold tend to hold water which steams while the copper is being poured.

The general question of defects in refined copper and their causes will be discussed more in detail in the next chapter.

The Furnace Cycle.—A normal cycle for a large modern furnace would be about as follows:

Charging	3 hours
Melting to "flatness"	5 hours
Recharging	1 hour
Melting to "afloat"	5 hours
Blowing	2 hours
Skimming	1 hour
Poling	2 hours
Pouring	5 hours
	24 hours

The fire is grated and rebuilt during the charging period.

Slag Formation.—The amount of slag made naturally varies with the nature of the charge. It is a minimum when melting straight cathodes. The addition of wire mill scrap at once increases it. In the anode furnace we have in addition to blister copper, black copper, silver building slag, liberator tank residues, cement copper, secondary scrap copper and miscellaneous clean-up material.

It is possible to melt cathodes in a basic furnace and keep the slag made down to a small fraction of 1 per cent of the weight of the charge. In order to do this care must be taken to keep clay used for luting up the furnace doors from getting into the bath and the fire must be so managed as to blow as little coal ash over as possible as it increases slag by uniting with copper oxide.

On the other hand, a foul anode charge may make 20 per cent of slag and still represent good work. Representative slag assays are given in Table 40.

TABLE 40.—REFINING FURNACE SLAG ASSAYS

Per cent	Copper	Iron	Nickel	Insoluble	Lime	Sulphur	Arsenic
Anode slag	40.51	5.30	6.99	38.74	0.25	0.17	0.21
Wirebar slag	48.55	2.99	....	41.73	0.53	0.19	

When nickel is present in quantity an infusible scoria is formed which carries with it a mass of metallics. Tin likewise forms a blanket of stannic oxide, which, however, can be fluxed.

Although the elimination of the elements occurs in the order of their oxidizability the separations are not sharp, and while a certain classification of impurities for further treatment can be roughly made, the losses in any such plan to separate lead, tin, zinc, etc., must necessarily be large, due to overlapping.

In the same way the copper slagged off carries with it some gold and silver. When anode assays over a period of time are compared with corresponding anode slag assays the silver appears too high. This is due to the large amount of silver brought into the charge in silver-building slags, which is not efficiently collected in the anodes but is passed on to the anode slag retreatment stage before it is again associated with the copper. Table 41 gives some assays where true comparisons can be made for both anode and wire bar furnaces.

TABLE 41.—RELATIVE SLAGGING OF GOLD AND SILVER

	Per cent copper	Oz. per ton silver	Oz. per ton gold
Anode slag	32.50	14.3	0.27
Anodes	99.44	81.48	2.299
Compensated slag assay	99.44	43.75	0.826
Slagging ratio	1.000	0.537	0.359
Wirebar slag	48.55	1.35	0.0140
Wirebars	99.94	1.40	0.0104
Compensated slag assay	99.94	2.76	0.0286
Slagging ratio	1.000	1.97	2.75

The surprising difference in the behavior of the wire bar furnace is due to the fact that the silver and gold in the cathodes is not alloyed with the copper but mechanically entangled as wandering anode slimes. Upon fusion some of this slime floats and is skimmed off with the slag. It is not all released, however, as we see not only by direct assay of the wire bars but from the lowering of electrical conductivity by one or two per cent when wire bars are compared with cathodes.

The general question of making anodes from foul material will be reserved for treatment in Chapter X.

Thermal Efficiency of the Refining Furnace.—The coal consumption of a large modern refining furnace under average operating conditions is about 12 per cent of the good product made. As the coal used in obtaining this figure runs about 13,750 b.t.u. per pound the heat requirement is 13,750 × 0.12 or 1650 b.t.u. per pound of copper produced.

If we take the mean specific heat of copper at 0.11 and the latent heat of fusion as 80 b.t.u. per lb. and assume that copper is charged at 70°F. and poured at 2170°F. we have the net heat input required $0.11 \times 2100 + 80$ or 311 b.t.u. per lb., giving an efficiency of $311 \div 1650$ or about 19 per cent. Waste heat boilers now recover heat equivalent to at least 6 lb. water from and at 212°F. per lb. coal burned in the furnace. This is equivalent to $966 \times 6 \times 0.12$ or 696 b.t.u. per lb. of copper, bringing the overall thermal efficiency up to $1007 \div 1650$ or about 61 per cent.

It will therefore be seen that operating as a simple reverberatory the furnace is very wasteful but that when there is a demand for steam the combined furnace and boiler is nearly as economical of heat as would be an electric furnace. The general question of waste heat boilers will be dealt with in Chapter XI.

Retreatment of Slags.—Slags made from normal anode and refining furnace charges require reduction with the substitution of another base to free the copper. As the slags from cathode charges carry very small values in gold and silver they are sometimes kept separate from the anode slags and the copper recovered therefrom made into casting copper in order to avoid the cost of passing this metal through the anode furnace and tank house steps of the process.

The simplest means of reduction is a small blast furnace operated with limestone and pyrites cinder as fluxes and making black copper as a product. A furnace much smaller than 44 in. × 66 in. gives trouble in keeping the crucible open and as even this small size has a capacity in excess of the requirements of most refineries, it is often necessary to run intermittent campaigns.

If true black copper is made—say 97 per cent copper carrying considerable iron—a very bad slag is inevitable, the copper running 2 or 3 per cent therein. As a rule there is enough sulphur in the iron flux used to produce a little matte, and a copper running about 94 per cent and a slag of 0.6 per cent is made. This product delays the work in the anode furnace unless it is systematically charged back day by day, as small quantities of sulphur take some time to blow out of an anode charge.

Where a smelter is operated in conjunction with a refinery, these furnace slags are usually added to the ore charge. The reducing action in a matting furnace is hardly strong enough thoroughly to decompose these high grade silicates and a noticeable increase in oxidized slag losses always follows their addition to the charge.

They are also very difficult accurately to sample on account of the metallics contained and the refinery will suffer and the smelter correspondingly gain unless special supervision is exercised over this sampling, as the workmen naturally avoid metallics in taking the sample as they give such trouble in the crushing.

Finally nothing is gained in cost by matting these slags, as the advantage of the larger scale of operation and somewhat lower slag losses is offset by the sampling costs and complication of adding sulphur to this high grade sulphur-free material only to blow it out again in the succeeding converting operation. The anode furnace gains somewhat however in not having any low grade black copper to treat.

Future Developments.—Great progress has been made in the development of the refining furnace and not much remains to be done along purely structural and mechanical lines. In twenty years the 24-hour charge capacity has been changed from 20 tons to 250 tons and furnaces of greater capacity could easily be built were there any justification for it. The copper is handled mechanically both in and out of the furnace. The hearth is now constructed of magnesite brick when a corrosive charge is to be handled. The walls and verb and sometimes the entire roof are now built of chrome or magnesite brick to withstand the copper oxide wash.

In firing the furnace there is yet some room for progress, but when it is considered that an open hearth steel furnace takes four times as much fuel per ton of product, it will be seen that there is not the same justification for expensive gas firing equipment. Either oil or gas firing may be successfully applied, however, and commercial factors may some day call for their introduction. The poling operation as already pointed out will doubtless in time be replaced by gas reduction.

Metallurgically the anode operation is quite satisfactory. The melting of cathodes is not in such good shape, however, as here what should be a simple melting is expanded into a complete refining. This has been attacked in two ways—by the use of the electric furnace and by continuous melting.

The electric furnace is not very promising as it has already been shown that with a waste heat boiler attached the heat efficiency of the reverberatory is high enough to give electric heat from steam driven generators a hopeless handicap. Then the high electrical conductivity of copper, the shape of the cathodes to be melted and the necessity of having the product absolutely free from bits of charcoal or other resistor material, introduce limitations in the design of the furnace.

It must also be remembered that there is a slight refining done in melting cathodes as shown by the concentration of impurities in the slag as well as the effective elimination of sulphur brought in as entrained sulphates from the electrolyte.

Continuous melting is more attractive. The method already described of charging large quantities of cathodes during pouring and carefully excluding all acid material from contact with the bath to avoid the formation of slag has been for some years in successful use and might be called semi-continuous melting. It is obvious that the principle could be extended until the amount charged just balanced the amount poured, but this requires slow casting rates in order to keep the heat up and introduces some practical difficulties. The sulphur is controlled in this method by inserting piles of cathodes which do not fully submerge in the molten bath. This gives the opportunity for a little oxidation of the exposed sheets before the mass softens and becomes immersed.

Various patents have been issued for plans which virtually combine a blast furnace melting with a reverberatory fore-hearth. Copper is so readily contaminated by contact with products of combustion, etc., however that it is difficult to apply methods of direct melting without having to go through a large part of the regular furnace treatment afterwards.

Perhaps the weakest point in the present reverberatory practice lies in the system of utilizing labor. Custom has placed a crew in charge of each furnace. Originally a night crew did the melting and rabbling and some of the poling while the day crew would attend to the ladling and charging. As a number of men were required for hand ladling this fitted in with the heavy work of charging. All the furnaces were supposed to be ready to cast early in the morning and the crew kept hours depending upon the furnace which would generally get progressively later during the week, the over Sunday period being used to catch up.

When mechanical ladling was introduced it became necessary to organize special labor gangs to assist in the charging of the furnaces which became much larger and with a reduced ladling crew.

Mechanical charging, however, eliminated this trouble and the necessary crew for handling a furnace is very small. The old system is therefore beginning to give way to one where instead of operating in unison the furnaces are intentionally staggered. In this way they may be skimmed one after another, for example, and a casting crew can be organized who will go from one furnace to another and be replaced by a new shift at a predetermined hour, making the men entirely independent of the behavior of individual furnaces. When this is fully accomplished furnace work will become a less arduous and less specialized occupation.

CHAPTER IX

THE REQUIREMENTS OF REFINED COPPER

In order to satisfy market requirements, prime electrolytic copper wirebars and cakes must possess high electrical conductivity, sufficient ductility and physical soundness. From the refiner's point of view the product must also be free from commercial quantities of precious metals. Ingots are given a little more leeway in conductivity and relieved of restrictions as to soundness, inasmuch as they are intended for remelting.

This general subject may advantageously be discussed under the headings of conductivity, pitch, ductility, castings and dimensions.

Electrical Conductivity.—It has come to be generally assumed that if a wirebar is a sound casting and a sample of the copper drawn into wire shows a satisfactory conductivity, the product may be accepted as prime electrolytic (or Lake) copper. This assumption is not strictly true, as will be shown later, but inasmuch as the preparation of the sample of wire for testing in itself demonstrates within certain limits the ductility of the copper, as the test may be easily and quickly made and as no other test appears to be of general application, conductivity will probably remain as the chief criterion of commercial copper.

Impurities in copper may be divided into three groups as regards their effect upon conductivity: Those which are insoluble in copper, those which are partially soluble and those which are completely soluble—remembering that we are interested only in mixtures where copper enormously predominates.

The elements which are insoluble can evidently have but little effect upon the conductivity, inasmuch as the total quantity of any one impurity is always far below 0.1 per cent and the impurity itself has a certain specific conductivity.

The class which is partially soluble exerts a very marked depression on the conductivity, as such elements form low melting point alloys with copper which crystallize out as eutectics, forming a matrix surrounding crystals of copper like the mortar joints of a mosaic. This matrix may be quite bulky, as part of the copper is added to the quantity of impurity present.

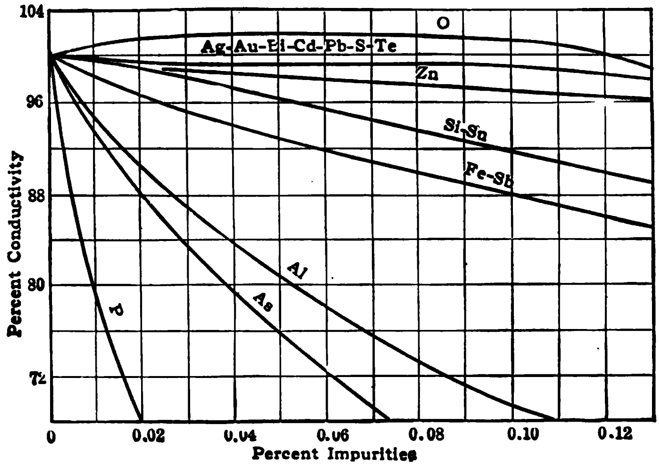

FIG. 27.—Effect of impurities on conductivity.

The few elements, such as silver, that form solid solutions with copper have a relatively mild effect upon the conductivity, which is quite negligible in view of the small quantities present.

About fifteen years ago the writer conducted a systematic investigation into the relation between impurities and copper.[1] Each element in question was added in varying amounts to crucible melts of high-grade copper wire and the conductivity of an annealed sample of wire drawn from the cast compared with the assay of the same wire for the impurity added. The results of this work are grouped together in Fig. 27.

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[1] *Trans.*, A. I. M. E., vol. xxxvi, p. 18.

It will be noted at once that the elements which are known to make copper brittle, such as lead, bismuth and tellurium, have but slight effect upon the conductivity, while those which make excellent bronzes, such as phosphorus, aluminum and silicon, have caused a marked depression. It is difficult, however, to make any practical application of these results, because the presence of one impurity often neutralizes the effect of another, and copper which would be expected to be of indifferent quality based upon these figures may prove to be excellent. This is the reason that chemical analysis, apart from the difficulties attending the accurate determination of traces of impurities, has proved of little value in judging copper as com-

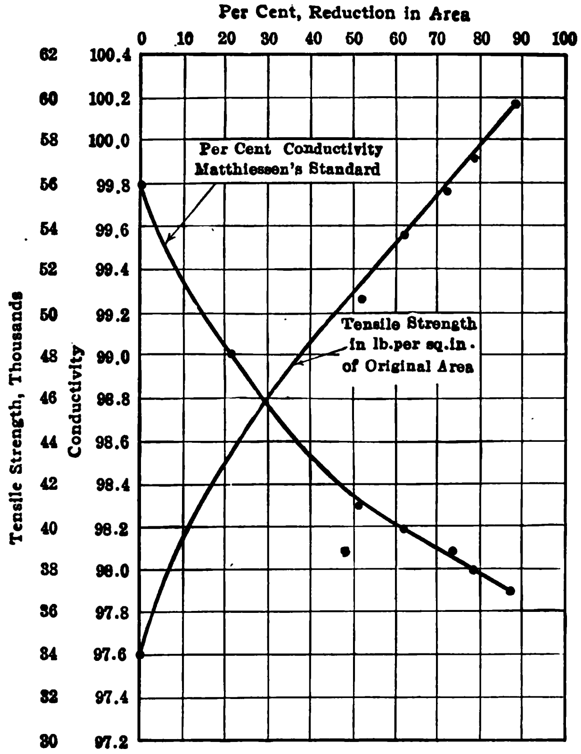

FIG. 28.—Annealed copper rod of different sizes drawn to No. 12 B. & S.

pared with the more practical test of forging and drawing followed by a measurement of conductivity.

By common consent conductivity has come to be expressed in percentage of the value of 0.141729 international ohm at 0°C. found by Matthiessen for a meter-gram of supposedly pure copper over fifty years ago. The specifications of the American Society for Testing Materials have established a minimum requirement equivalent to 98.5 per cent for wirebars and cakes and 97.5 per cent for ingots,

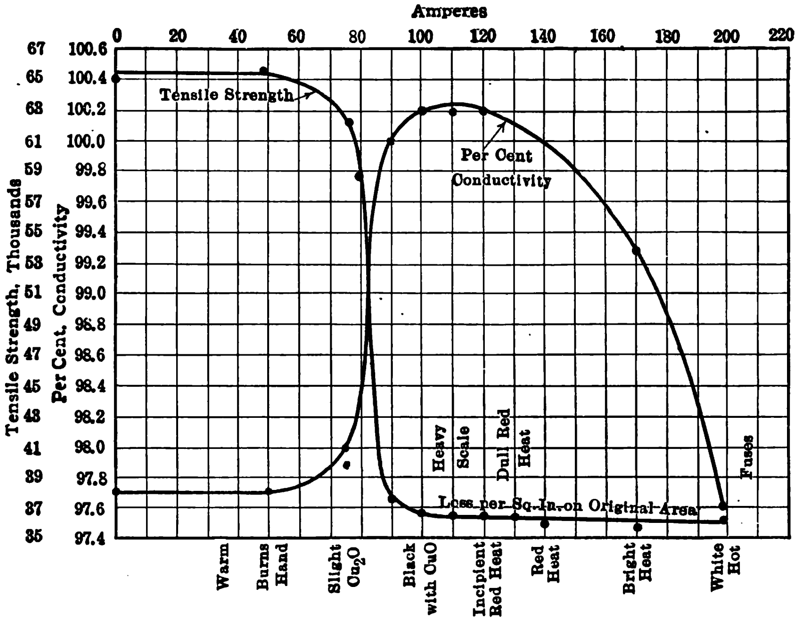

FIG. 29.—Electric annealing of No. 12 B. & S. copper wire.

determinations being made upon annealed samples. Average copper on the market runs considerably higher than these figures, much of it being over 100 per cent as compared with the imperfectly purified standard copper of Matthiessen. The purest cathode copper—that is, an annealed sample of wire drawn directly from a cathode without melting—may run over 102 per cent; it is unusual, however, for copper that has been melted to run over 101 per cent. The lowering of conductivity by melting is due chiefly to the fact that much of the impurity content of the cathode is present merely as mechanical contamination, a certain proportion of which a melting will incorporate chemically. Then there is always the opportunity for the copper to absorb impurities from outside sources during furnace refining.

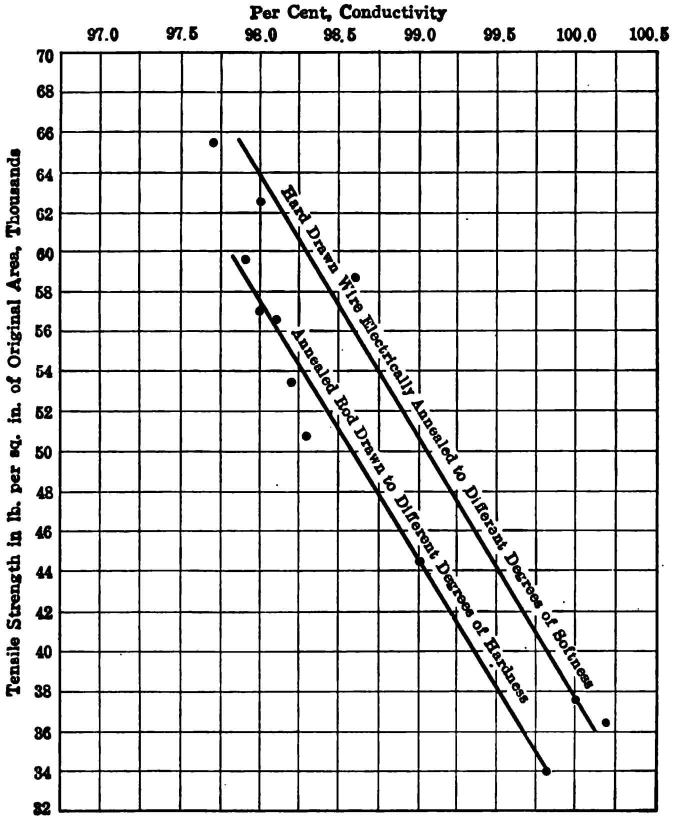

FIG. 30.—Relation between conductivity and tensile strength in copper wire.

In drawing copper into wire the coarse crystalline structure of cast copper is broken down into a fibrous structure much harder and stronger but of a lower electrical conductivity, due perhaps to a rearrangement of the system of series-parallel circuits made by copper crystals and matrix. The depression of conductivity bears a direct relation to the degree of hardness attained, as shown in Figs. 28, 29 and

30.[1] It will be seen from Figs. 29 and 30 that the softening of a wire by annealing has a progressive character in the exact reverse direction from the hardening by working the metal.

In order to arrive at a definite standard for comparing conductivities, therefore, wire is annealed in order to obliterate the somewhat uncertain effect of hard drawing before a determination is made. On the other hand, either a partial annealing or an overheating or "burning" of the wire will give results below the truth. It is therefore necessary to bring the wire to incipient red heat (about 900°F., or 480°C.) for a brief time in order to get consistent results. All errors, however, are on the safe side, as it is impossible to get unduly high conductivity by faulty manipulation.

Pitch or Set.—The pitch, or set, of copper is an expression used to define the appearance of the free surface of a cast copper bar; that is, the bar may be of high, normal or low pitch or it may be "in set" or "out of set."

Molten copper readily dissolves the various gases with which it is brought in contact in the refining furnace, such as oxygen, carbon monoxide and dioxide, and sulphur dioxide. As the copper cools and sets in the mold excess gas is given off, and the proper control of this phenomenon is the secret of good furnace refining. As has been outlined in the last chapter, the bath after melting is allowed to oxidize and the resulting cuprous oxide dissolves and acts as a scorifying agent, the scoria is skimmed off and the excess cuprous oxide reduced by poling. A button of copper cast in a "say-ladle" gives a characteristic set surface and fracture for each stage, the finished product showing a slightly swelling surface without deep wrinkles and a rose-red silken fracture. Should the poling not be carried far enough, the set surface will show a depression and the metal will be hard and somewhat sonorous. Metallographic examination will show thick veins of cuprous

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[1] See Addicks, *Trans.*, American Institute of Electrical Engineers, vol. 22, p. 695.

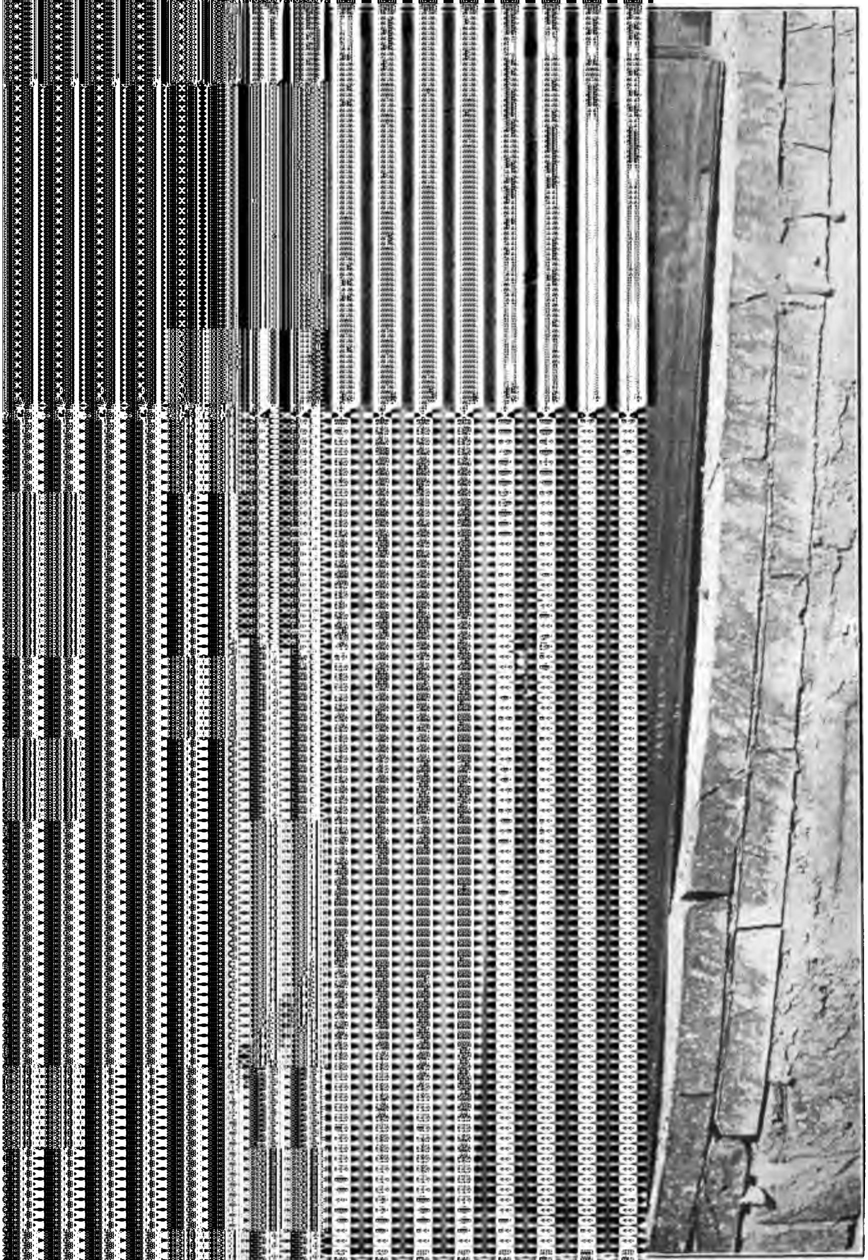
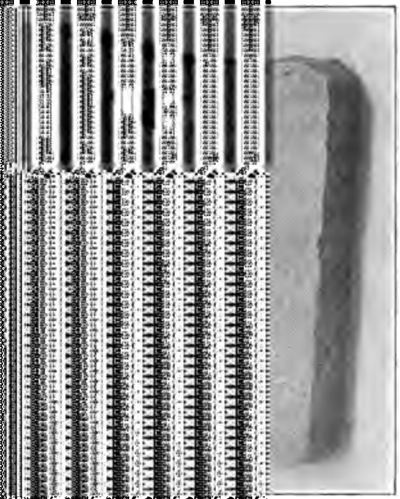


FIG. 31.—Gas cavities in improperly refined bar.

close to the sides where wrinkles should be fine

at more dissolved oxide rope it was at one time off before rolling when et.



low set bar.

at the addition of exceed- elements, such as lead, copper so red-short as to impossible to state per- account of the neutraliz- ies which may or may not to say that nearly all raced to low pitch.

can be hot rolled into ling free of scale can be without any intermediate there is always a certain e-drawing machines, and to bear a direct relation to the copper contents of the lot of wirebars under test. It is, therefore, customary to impose, in addition to the conductivity specification, a requirement that the copper content (including silver) shall not be less than 99.88 per cent, a figure intended to represent a limit of 99.90 per cent after allowing a margin for assay precision.

The determination of traces of impurities in copper requires long experience. This is particularly true in the case of sulphur, where even the atmosphere of the laboratory must be free from sulphur compounds.

Mechanical tests on samples of wire as checks upon the character of the raw copper have been abandoned because the fabrication of the wire introduces so many variables. The former tests, as a rule, consisted of measurements of tensile strength and torsion.

Tensile Strength and Torsion.—The tensile strength of copper wire depends upon the percentage of reduction in area after annealing, the speed and the temperature of drawing. With proper regard to these factors, almost any copper not too brittle to draw can be made to fulfill standard telephone wire specifications as to strength.

The usual torsion test was to determine the number of twists a No. 12 B. & S. (2.05 mm. diameter) hard-drawn wire would stand before snapping. This test is perfectly worthless, because it depends entirely upon the properties of the thin skin which forms on wire in drawing. A wire as it comes from the drawbench when put in the testing machine will twist uniformly throughout its length for a few turns and then twist tightly at one point and snap. If the wire is scoured with emery paper or dipped for a moment in nitric acid before twisting, the skin is broken down and before snapping the entire length will coil tightly, giving several times the number of total twists formerly obtainable. This skin is at least in part due to imperfect pickling after rolling, as by the use of a nitric acid instead of sulphuric acid pickle on the rod the number of twists that the wire will stand is greatly increased. Particles of oxide scale are probably rolled into the metal, and sulphuric acid, while it will dissolve oxide, cannot cut metallic copper to reach it.

Sometimes bars are badly overheated in the heating furnace before rolling, and this probably causes absorption of gases and consequent brittleness. Altogether, mechanical tests have been entirely dropped as a check on the quality of the copper as distinguished from the finished wire.

Castings.—In order to get a perfect casting from a physical point of view, the first requisite is that the copper should be in correct pitch, a subject which has already been discussed at some length. Small adjustments in pitch are made by adding or removing charcoal at the casting machine ladle. Next, the temperature of the copper must be high enough to insure good fluidity without burning the mold. The mold itself must be warm—that is, slightly above the boiling point of water—in order to avoid any condensation of moisture or too sudden chilling of the copper first striking it. There must be a fine film of a suitable mold wash to prevent sticking and the material used must be free of any volatile matter. The mold must be solid and free of pores which would entrap water; otherwise a spongy casting would result. The copper must flow in quickly but evenly and the casting machine must operate so smoothly that a partially set bar will be subject to no vibration or jars. The bars must be quenched in water soon after setting and this water must be warm. Finally, the molds must be free of warp and set truly level and filled to a given mark without any attempt at adjustment.

These many small points require very careful supervision at the casting wheel and carelessness in any one detail will give more or less defective product. Bars may be out of size, out of set, porous or contain splashes, fins, cold sets or "fish."

Out-of-size bars result from out-of-level or warped molds, or from careless filling to a wrong level. Too large a bar may result in the production of fins in the rolls, due to crowding. Molds suspended at the ends tend to drop in the middle and pinch at the top center.

Porosity may come from low set or may be due to moisture. It generally follows cold or porous molds or too high a casting temperature. In this connection it may be stated that copper molds turn out superior castings to iron ones, although the latter are more or less in use.

Splashes occur when the copper first strikes the mold, being thin sheets of metal which splash on the sides and freeze. Unless they are knocked off with a suitable tool before they are submerged, they are likely to leave a cold set or unwelded lamination in the bar.

Fins are sharp high edges due to filling the mold too rapidly or to vibration of the casting machine giving a wash to the bar before setting. They must be chiseled off the finished bar or they will be rolled in later.

Cold sets occur in various ways whenever molten copper is allowed to enfold cold splashes, etc. They must be chiseled out or, if extensive, the bar rejected.

Fish are bits of charcoal, nails or other foreign bodies allowed to become incorporated in the casting. They are supposed to be removed by a "fisher" during pouring much as a fly is rescued from a glass of milk.

The color of cast copper depends chiefly upon the time allowed to elapse between pouring and quenching and the temperature of the bosh water. The beautiful ruby shades are due to thin films of the lower oxides, and a slight change from the proper conditions will make bars either brassy or black. Twenty years ago good color was given great importance at the rolling mill, but it has nothing to do with the quality.

Dimensions.—Each refinery issues a metal schedule giving the weights and dimensions of the market shapes it produces. This covers wirebars, cakes, ingots, ingot bars and billets. Very large wirebars, very heavy cakes and billets cast on end are poured by hand from a crane ladle and the additonal cost over machine casting is reflected in a premium charged. Ingotbars are merely three ingots cast end to end in order to bring the weight up to a figure where steamships will accept them without demanding that they be barreled.

No rigid requirement as to regularity of size and weight is required of ingots and ingotbars which are to be remelted. In the case of wirebars, however, the American Society for Testing Materials specifications give a tolerance of 5 per cent in weight and ¼ in. in any dimension except that wirebars may vary 1 per cent in length and cakes 3 per cent in any dimension greater than 8 in.

For wirebars, each refinery has its own design and proportions of point. Different rolling-mill men have such contradictory opinions regarding the relative advantages of slight changes in these matters that it is probable that one design is about as good as another. A long point enters the roll more easily at the first pass, but is apt to leave more scrap. A square cross-section is desirable, because a flat bar is apt to turn over in the rolls when part way through. The first pass is often a box roll and after that diamond and oval alternately.

American Wirebar Sizes.—A refinery carries about six sets of standard molds and varies the weight of the bars cast from each set by suitably changing the depth to which the molds are filled within the limits imposed by the necessity of keeping a bar reasonably square in cross-section. An example from practice is shown in Table 42.

TABLE 42.—TYPICAL AMERICAN WIREBAR SIZES

Weight, lb.	Length, in.	Depth, in.	Top width, in.	Bottom width, in.
135	35¼	3⅞	3¾	3 5/16
175	47½	3¾	3 11/16	3¼
200	49½	3⅝	4	3¾
225	50	4 1/16	4	3¾
250	56	3⅞	4⅛	3 15/16
275	55⅜	4 1/16	4½	4⅛
300	55½	4⅜	4½	4⅛

Bars of 135 lb. and under are commonly used in Europe, but practically not at all in the United States, where the usual demand is between 175 and 225 lb. Very heavy bars, running around 800 lb., are in moderate demand on the Continent for making great lengths of trolley wire without reverting to the American practice of brazing.

Inasmuch as the great demand for power in a rolling mill is in the first two or three passes, the roller would prefer a long bar of small cross-section. This, however, would increase the difficulties in casting and in obtaining sound bars, and developments in this direction are improbable unless it be in connection with castings made on end.

Cakes are the most troublesome class of castings to make. They have a large set surface and this is rolled out to a mirror-like finish where every flaw is readily seen. Often they are cast on "mixed" rings, so that wirebars are interspersed on the mold ring and, as perfect pitch for a wirebar is not necessarily perfect for a cake, a slight disadvantage results. It is quite impossible to cast a small ingot and a heavy cake from the same ladle without adjustment in pitch, as the shrinkage and gas release conditions are so different in the two cases.

Occasionally copper is shipped as cathodes in place of ingots. This is a perfectly logical procedure, as the furnace operation is not a true refining and it has been abundantly shown that a cathode really freed from electrolyte can be melted to high-grade copper without any furnace refining whatever. On the other hand, the cathodes must be sheared to a suitable size, they are often brittle and there is always more or less metal loss in transit. Aside from nodules being dropped by the wayside, pieces are easily broken off by thieves. Also cathodes are quite variable in individual quality, while in the refining furnace thousands are averaged together. The result is that ingots still hold their own in the brass trade, although a fair proportion of cathodes are sold on an allowance below the price of wirebar copper.

CHAPTER X

COPPER FROM SECONDARY MATERIAL

In addition to the cirulating products incident to normal copper refining, the plant is often called upon to treat a wide range of metallurgical by-products from outside sources as well as miscellaneous copper-bearing scrap material. Now that matte smelting plants exist on the Atlantic seaboard, there is little reason to consider anything in the nature of ore or matte, but the following list of materials is fairly representative of what offers:

A. Junk.
  a. Lamps, clocks, etc.
  b. Borings and chips.
  c. Wire.
  d. Sweepings.
  e. Coins and alloys.
B. Mill Products.
  a. Wire.
  b. Scale.
  c. Cement.
  d. Stampings.
C. Metallurgical Products.
  a. Cement.
  b. Amalgamation plates.
  c. Secondary pig.
  d. Nickeliferous pig, black copper, etc.
  e. Furnace bottoms.
D. Refinery By-products.
  a. Silver refinery slags.
  b. Liberator tank cathode products.
  c. Flue products.

There is a surprisingly large tonnage of such miscellaneous material available, and of course a good deal of it is absorbed by relatively small sweep smelters, who generally feed it indiscriminately into a small blast-furnace, making a foul pig which is sometimes given an additional reverberatory treatment and sent back to the market as casting copper and sometimes is sold to an electrolytic refinery. Such work is a very disturbing element in a copper refinery unless the tonnage accepted is great enough to warrant the establishment of regular facilities for handling it. The general questions involved are, first, sampling; second disposition; third, proper furnace construction; fourth, possible saving of impurities as by-products.

Sampling.—The sampling of junk is an art in itself. The ordinary junkman, who travels around in a wagon buying what offers, learns in time to make very close estimates of the metal values of such material, but the refinery cannot afford to let its sampling department adopt such methods on general principles.

The first rule in sampling junk is to classify the material. The insulated wire is put in one lot, the bare wire in another, the alarm clocks and automobile lamps in a third, the sweepings in a fourth, the borings in a fifth, and so on. Clocks and lamps have been considered as a class because they are one of the staples of the junk business. Occasionally large lots of Oriental bronze coins come into the market. A noteworthy instance of this was when Japan took over the control of Korea and exported about 6,000,000 lb. of Korean "cash."

The second step in the sampling is to endeavor to get a representative part of each classified pile. Coins or sweepings can be quartered down like so much crushed ore. Wire can be clipped here and there. Borings can be reasonably sampled by selection. The remainder can be handled only by intelligently taking grab samples, and this requires experience and skill.

The third rule is always to take duplicate samples and to hold the lot intact until assays are out, giving an opportunity for resampling if the assays show sufficient lack of agreement to indicate poor sampling.

The next step varies according to the nature of the material. With dirty metallic material, such as wire or borings or sweepings, a burning loss should be obtained by soaking with gasoline where necessary and igniting, noting the weight before and after. With miscellaneous manufactured material, where different metals are used, as in a clock, or containing solder, as in a teapot, the only way is to make a crucile melt of a rather large sample, accounting for the bar, slag and crucible absorption. Often a material has to be sorted into metallics and dust, as in the case of some sweepings. In general, therefore, it will be seen that sampling junk is a tedious and expensive business. Most junk carries some gold and silver values arising from jeweler's sweeps, etc.

Mill products, such as scrap wire, punchings, etc., shipped directly from the wire mill or other factory to the refinery, are much easier to sample. Here the material is already classified and relatively clean. Care must be taken to see that no bimetallic wire has inadvertently found its way into straight copper wire bundles. It would be thought that bright copper wire from primary sources would need no sampling, but there is always more or less grease attached to it, and the true copper content is nearly always several tenths of 1 per cent below standard. Tinned wire will run 1 per cent or more low and bimetallic wire may run 40 per cent low. The refinery in turn makes a small profit in that the wire bars sent out and accepted by the trade as 100 per cent copper in reality run seven or eight hundredths of 1 per cent below this.

Among the metallurgical products two require special mention, amalgamation plates and furnace bottoms. Amalgamation plates are copper sheets which have been amalgamated on the surface and used to collect gold and silver values from finely crushed native ores. The amalgam has been thoroughly scraped off before the plate is scrapped on account of wear or other defect, but nevertheless sufficient gold is retained to make such material relatively valuable. In this case it is necessary to shear the plates up into equal squares of a few inches on a side; then take systematically say every tenth square, following such a system of reduction until the sample is small enough to permit of crucible reduction.

Furnace bottoms are very troublesome to handle. They are generally received in large masses which cannot be drilled or broken. They are usually placed in a furnace for treatment by an overhead crane at a time when the roof is out for rebuilding. They cannot be blasted or cut apart and the only way to reduce the size of a large piece is to build a small flue across the top and channel with a hot oil flame.

The only way to sample them is therefore to chip around the edges. Unfortunately they are often quite rich, as silver and gold tend to concentrate in furnace bottoms. The refiner has to make an allowance in the treatment terms to cover the sampling danger when handling such material.

Disposition.—There are several places in the process where secondary material can be introduced. The first is the slag cupola, the function of which is primarily to treat the anode and wire bar furnace slags and which always has capacity to spare. Nearly anything in the scrap line can be introduced here, but it does little more than extract the metals contained and put them into compact shape. Their chemical treatment requires oxidation, which cannot be obtained in the strongly reducing atmosphere of a black copper cupola. Plants treating junk exclusively usually make a blast-furnace melting their first operation, using some briquetting or sintering apparatus to take care of the very fine material before charging.

The usual point of entry is the anode furnace. This insures saving the silver and gold contents and getting the copper in electrolytic form, neither of which is possible to the small junk smelter.

There are certain objections to introducing such material into an ordinary anode charge. In the first place, it is usually in such shape physically that it will take up a disproportionate amount of space in the cold charge. This can be met to a certain extent by charging it at the recharge period when there is plenty of room in the furnace. Then impure material delays the blowing and skimming, and it is important that the furnaces operate on schedule time. Finally, quicker work and better elimination of impurities as well as a better slag concentration for possible by-product recovery are made by treating impure material without dilution. This leads to setting an anode furnace apart for special work at least part of the time. This has another great advantage in that it allows direct costs of the work to be kept.

Then we have the refining or wire bar furnaces. Nothing should be added to a cathode charge regarding which there can be any question as to quality. It is customary to include as admissible, however, scrap wire baled in "cabbages" which originates at standard wire mills. In ingot charges, where conductivity requirements are not quite so strict, liberator cathodes from the first row of tanks in the purifying system may be added with discretion.

Finally, we have the possibility of using a special refining furnace for the production of casting copper. This is attractive in that it enables material which is practically free of silver and gold and high in copper—scrap brass for example—to be worked directly into a marketable product. The disadvantage is that casting copper has no stable market. It always sells at a discount and at times is nearly unsalable.

Furnace Construction.—Until recent years the standard refining reverberatory has been constructed of silica throughout. In some special cases a silica brick bottom has been employed, but the usual construction was silica sand bottom with silica brick sides and roof. Such a furnace is built with a cooling vault, cast-iron bottom plates mounted on brick piers, and a false bottom of fireclay brick. The vault should be arranged with consideration of a possible runout of copper through the bottom. It is desirable to lead the molten copper away from the vault before it sets, so that it can be recovered without tearing down the entire furnace, but it is equally essential to see that it does not run into the casting wheel pit or ash pit where it will probably come into contact with water and cause serious explosions. When a break-out occurs the proper thing to do is to charge cold copper into the furnace to set the charge, which is not difficult on account of the high heat conductivity of copper; but if explosions are occurring it is not safe to approach the furnace.

A sand bottom must be carefully impregnated with copper, and an excellent way in which to accomplish this is to mix the sand with about 30 per cent of its weight of copper oxide scale. This is thoroughly turned over and shoveled into the previously dried furnace, where it is calcined at a moderate heat for about 12 hr. The fire is then dropped and the floor carefully leveled and tamped down. The furnace is then fired at maximum temperature—perhaps 2700°F.—for 24 hr. and the furnace after cooling is ready for a small seasoning charge of scrap wire or similar light material. This charge, amounting to perhaps 10 per cent of the rated capacity of the furnace, is melted and ladled out, and after another brief cooling, one twice as large is put in. After this has been ladled the furnace should be ready for service, although it should not be crowded for a few charges, starting at 50 per cent capacity and working up.

This furnace, even when treating high-grade material will be more or less fluxed by the cuprous oxide of the charge, the silica of the slag being taken chiefly from the bottom of the walls near the metal line. The old treatment for this was "fettling," or plastering corroded spots with fire clay, after each charge was cast.

Prolonged heating in the treatment of foul charges is apt to smelt some of the bottom of the furnace, and when pieces of the bottom begin to "float up" there is always danger of a run-out. Also if elements such as lead are present in appreciable quantity the litharge formed will hungrily attack the silica of the furnace. In fact, a good silica furnace can be easily ruined by a single charge of leady copper. More than 2 per cent lead is always cause for great anxiety.

After a while magnesite and chrome brick were tried as a lining material for the walls of the furnace near the metal line. Approved practice was the use of magnesite for the zone protected and the introduction of one course of chrome brick between the magnesite and silica of which the wall was continued up, the chrome acting as neutral material between the basic and acid bricks.

Magnesite brick spalls badly when exposed to sudden temperature changes. Chrome brick is not subject to this objection, but fails because of softening when exposed to heavy thrust when highly heated. Chrome brick is more difficult to smelt for recovery of metal values.[1]

The next step was to use a chromite verb with great gain in heat control of the furnace, since small dimensional changes from the cutting away of the verb cause great differences in the characteristics of a furnace.

Then the complete basic furnace was developed with magnesite bottom and chrome walls and roof.[2] The sand bottom furnace is constructed with the bottom inside the walls; the basic brick furnace is built with the walls standing on the bottom in order to carry the thrust of the inverted arch directly through to skewbacks reacting against the brickstaves.

With complete basic furnaces it has been found possible to treat material high in lead, and which may require heavy firing for several days without damage to the furnace, so that clean anodes may be made from foul sources of supply.

By-Products.—Tables 43 and 44 give an idea of the character of some of the low-grade material offering in quantity.

An examination of these analyses shows that aside from copper, the main value, there are often present considerable quantities of gold, silver, arsenic, nickel, cobalt, lead, zinc and

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[1] Pyne, *Trans.* A. I. M. E., vol. 59, p. 151.

[2] Addicks and Brower, U. S. Patents 1083719 and 1148814.

TABLE 43.—ANALYSES OF CEMENT COPPER

Source	Oz. gold	Oz. silver	Per cent copper	Per cent iron	Per cent insoluble
United States.......	Trace	3.6	80.93	1.40	8.80
United States.......	0.01	5.3	71.53	1.30	17.06
United States.......	0.28	11.0	60.58	10.00	1.68
Australia...........	0.45	0.32	78.28	3.97	3.50
England............	0.05	19.8	76.62	5.20	1.63
Belgium............	Trace	0.40	69.51	8.50	2.24
Unknown...........	Trace	0.20	32.18	26.02	5.99

tin. Where gold and silver are present in sufficient quantity to pay the cost of electrolytic treatment, the furnace product should obviously be anodes. Where the silver and gold values are low, casting copper may be considered as a product, but the time required for refining, market deduction for casting copper, values and costs must be carefully balanced in making a decision.

Arsenic can be almost totally removed from an otherwise pure bullion as sodium arseniate by fluxing with soda ash. This method is employed in the Lake district, the soluble salt being leached out of the slag with water.

When any of the other impurities are present in quantity, we may consider the possibility of their recovery in slags, in flue products or through the electrolyte purifying plant In the formation of slags the elements oxidize in the order of their basicity. Their relative affinities for oxygen may be judged by the heats of formation of their common oxides, as follows:[1]

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[1] Values from Richards' "Metallurgical Calculations."

Au_2O_3..................	−11,500	CoO..................	+ 64,100
Ag_2O..................	+ 7,000	FeO..................	+ 65,700
CuO..................	+37,700	ZnO..................	+ 84,800
PbO..................	+50,800	SnO_2..................	+141,300
NiO..................	+61.500		

TABLE 44.—ANALYSES OF FOUL COPPER BULLION

Material	Source	Oz. Au	Oz. Ag	Per cent Cu	Per cent Ni	Per cent Co	Per cent As	Per cent Sb	Per cent Bi	Per cent S	Per cent Fe	Per cent Pb	Per cent Se	Per cent Te	Per cent Zn	Per cent Sn	Per cent insol.
Black Cu......	Australia......	0.24	2.0	.....	0.89	....	0.22	0.20	0.06	0.86	0.01	......	0.01	0.01			
Black Cu......	Africa.........	0.003	0.15	90.25	Trace	5.59	0.10	.....	....	1.32	2.05	None					
Secondary Cu..	United States..	0.12	7.8	84.77	0.24	....	0.04	0.23	None	0.55	3.19	3.09	Trace	Trace	3.17	2.07	0.56
Blister........	United States..	0.40	9.0	97.80	1.28	....	0.002	0.003	Trace	0.04	0.07	0.005	0.08	0.006	0.03	....	0.14
Black coins....	Korea.........	0.08	6.2	67.48	....	....	2.15	0.06	0.01	....	1.87	24.10	Trace	....	4.27	....	0.08
Yellow coins..	Korea........	0.12	5.9	56.73	....	....	0.47	1.15	0.03	....	1.35	9.31	....	....	30.81	1.02	0.18
Secondary Cu..	United States..	0.09	6.2	85.01	0.35	....	0.03	....	....	0.94	0.92	5.49	....	....	1.60	4.21	0.11
Secondary Cu..	Europe........	.....	....	75.66	0.40	....	....	0.15	....	....	0.89	2.37	....	....	19.12	1.38	

From these figures we should expect to get first the tin, then the zinc, then the group of cobalt-nickel-iron, and finally the lead, leaving copper-silver-gold in the metal bath. In practice, however, we have to consider the fusibility of these oxides and the readiness with which they form silicates. The situation is quite different from ore smelting in that we are dealing with metallic alloys and always in the presence of a preponderating amount of copper.

The possibility of recovering tin from secondary copper such as given in Table 44 is indicated in Table 45 which gives a metal balance on one anode furnace charge.

TABLE 45.—TIN RECOVERY

Input

Material	Weight	Per cent Sn	Contents
Crude bullion	53,567	3.19	1,709
Crude bullion	50,874	3.30	1,679
Crude bullion	61,125	2.07	1,265
Crude bullion	51,918	2.23	1,158
Crude bullion	54,027	2.10	1,135
Crude bullion	54,440	3.02	1,644
Furnace returns	6,000	0.27	16
Anode scrap	30,000	0.15	45
Total	361,951	2.39	8,651

Output

Material	Weight	Per cent Sn	Contents	Per cent Sn input
Anodes	278,801	0.61	1,701	19.7
First slag	7,686	0.38	29	0.3
Second slag	17,796	0.78	139	1.6
Third slag	39,657	14.43	5,722	66.2
Metallics	4,019	0.61	25	0.3
Unaccounted for	13,992	.....	1,035	11.5
Total	361,951	.....	8,651	100.0

There has been collected in the third slag 66 per cent of the tin.. If we take the copper in this slag at 25 per cent, we shall have upon reduction to metal a foul alloy running 30 to 35 per cent in tin, a reasonable first step toward the recovery of this metal.

Zinc is not a sufficiently valuable metal to warraut the cost of its extraction from impure or low-grade products. Inasmuch as a copper furnace is operated at a temperature above the boiling pint of zinc, it would be possible to make a certain recovery as fume, but as this would be contaminated with other volatile impurities such as arsenic and antimony present in foul bullion, such an operation would have no commercial standing.

While iron, cobalt and nickel stand close together in the heat of oxidation scale they show a marked difference in slagability. In fact the ease of removal in a reverberatory furnace might be arbitrarily indicated as 1.00 for iron, 0.10 for cobalt, and 0.01 for nickel.

This is illustrated in a general way by some published[1] data of experiments conducted in a 2-ton furnace at the Wysk smelter in Russia, some of the results of which are shown in Table 46.

Iron is of course far too cheap a metal to be considered as a by-product except in very large-scale ore smelting

TABLE 46.—RELATIVE SLAGABILITY OF IRON, COBALT AND NICKEL

	Original bullion	After first refining	After second refining
Copper, per cent	99.55	99.42	99.66
Iron, per cent	3.04	0.011	0.008
Cobalt, per cent	0.894	0.023	0.024
Nickel, per cent	0.408	0.110	0.109
Iron	1.000	0.004	0.003
Cobalt	1.000	0.026	0.027
Nickel	1.000	0.270	0.267

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[1] Hofman's Metallurgy of Copper, p. 391.

operations. It can be easily removed from copper bullion by slagging, but not without the coincident removal of a small amount of the copper as cuprous oxide, which forms the scorifying agent.

Cobalt can be removed with reasonable facility in like manner and collected in a slag running perhaps 20 per cent cobalt and 20 per cent copper, but truly cobalt-free copper could not be produced without slagging a large amount of the copper in repeated scorifications.

Nickel is much more difficult to deal with, and is generally recovered by separation as a soluble sulphate in electrolytic refining. Considerable data are available on its behavior in the anode furnace. An example of some large-scale experiments is given in diagrammatic form in Fig. 33, and these curves are analyzed in Table 47.

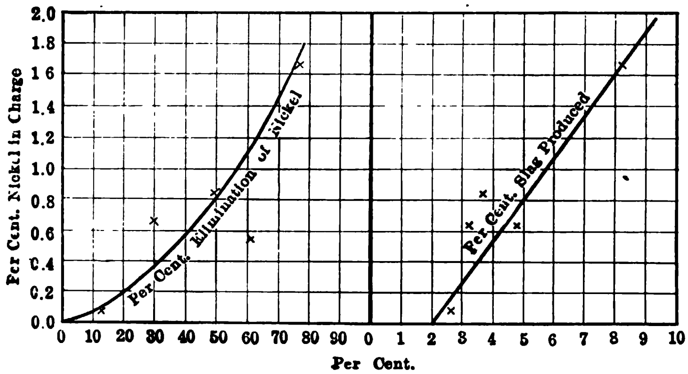

FIG. 33.—Behavior of nickel in the copper reverberatory.

TABLE 47.—BEHAVIOR OF NICKEL IN THE COPPER REVERBERATORY

	Per cent				
Nickel in charge	0.0	0.5	1.0	1.5	2.0
Elimination	...	37.2	57.0	70.0	80.4
Nickel in product	0.0	0.32	0.44	0.45	0.40
Slag	2.0	3.8	5.7	7.6	9.4
Nickel in slag	0.0	4.9	10.0	13.8	17.1

It is evident that more prolonged working of the charges richer in nickel would result in a somewhat lower nickel in the product and a larger quantity of slag lower in grade as to nickel, but is it quite out of the question to reduce the nickel tenor of a large charge to the degree shown by the small Wysk furnace. The slag, if treated in a matting furnace for the recovery of copper, will lose a large part of its nickel to the new slag; if treated in a black copper cupola, the nickel will be nearly all reduced with the copper.

Lead is readily separated from molten copper as litharge. As this active base rapidly attacks siliceous material, quite small quantities of lead demand a basic furnace for safe handling. Lead is practically insoluble in pure copper, but in the presence of sulphur or various impurities it is absorbed, and considerable quantities are found in secondary copper and occasionally in blister where leady copper ores have been treated. Certain bearing metals are made of a mixture chiefly of copper and lead, and the black Korean coins listed in Table 44 showed high percentages of lead. When melting down large quantities of these in a furnace with a basic brick bottom placed over a cooling vault, it was noticed that practically pure lead sweated through the bricks underneath, indicating liquation and a possible means of separating lead from copper. A copper-lead slag which can be profitably smelted for both metals is readily made from such material.

In general, electrolytic refineries recover a large part of any nickel or lead entering their plants in sufficient quantities, and steps would be taken to recover cobalt and tin did the crude copper carry sufficient of these metals, but the disturbance of the process due to interference of these impurities in the main business of copper refining overshadows the possibility of placing impurities on a revenue-producing basis except where large regular quantities have to be dealt with. Where casting copper is made, a portion of these alloy impurities remains and actually improves the copper for certain purposes by increasing its fluidity or altering its color.

CHAPTER XI

THE POWER PROBLEM

An electrolytic copper refinery may obtain its power from a self-contained steam or gas plant, from an adjacent water power or by transmission, but while each case will call for a different type of power plant as far as the provision of current for the tanks is concerned, the demand for fuel for smelting and for steam for heating liquors will remain unchanged. The fact that both fuel and steam are required introduces waste heat boilers in any event and most refineries have steam driven electrolytic generators, although there are notable exceptions. The conditions surrounding each case call for individual study of all the factors entering and it is the purpose here merely to point out the general requirements and limitations of the problem as a whole.

In the early plants, before the days of waste-heat boilers and with live steam heating, the total water entering the plant could be considered as utilized roughly one-third for generation of electrolytic power, one-third for steam for heating and miscellaneous uses and one third for make-up water in the tanks and at the boshes. The ideal steam driven plant would, therefore, be one where the steam generated by waste heat at the reverberatories would be sufficient to supply the demands of the engine room, the exhaust from the engine room was used for heating and the condensate finally was used as make-up water at either the boshes or the boilers. This ideal solution is yet far from being reached but the very uniform conditions of load and output under which a refinery is run has enabled sufficient progress to be made in this direction considerably to handicap hydroelectric and gas plant competition.

Waste Heat Boilers.—It is perhaps most logical to start with the consideration of the amount of steam available as a by-product at the reverberatories.

Given a fair grade of bituminous coal a modern refining furnace will average eight to nine tons of product per ton of coal burned. As there are two furnace operations and as the anode furnace treats some 15 per cent of anode scrap and various other items contribute to swell the net tonnage treated in either furnace, a ratio of four to one is safe, giving 25 per cent fuel consumption on a cathode basis.

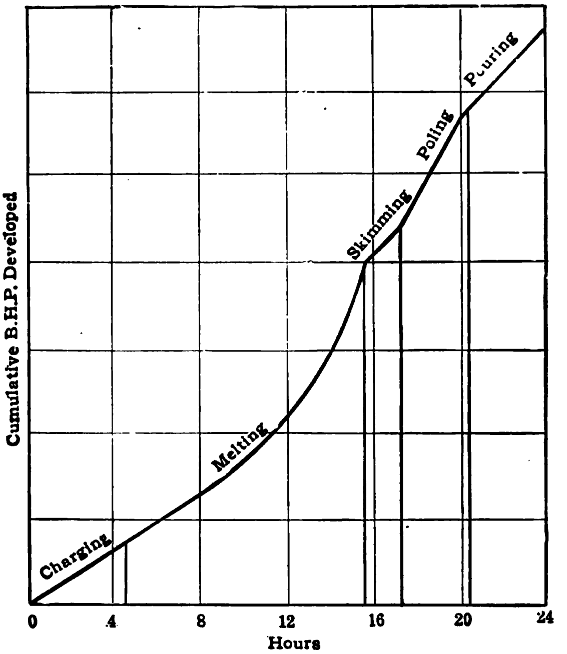

FIG. 34.—Steaming rate of waste heat boilers.

A properly designed boiler, placed close to the throat of the furnace and equipped with an economizer can be depended upon to give an average equivalent evaporation of between six and seven pounds of water per pound of coal fired. We, therefore, have available about 1.5 lb. of steam per pound of cathode output, or in other terms a 200-ton furnace will develop at least 363 boiler horse-power.

The rate of steaming is not uniform as although the coal in a large modern furnace is consumed quite steadily throughout the twenty-four hours, the two extremes of poling and charging give large differences in the temperature of the gases leaving the furnace. The situation is graphically expressed in Fig. 34. Where a number of furnaces are feeding boilers in parallel their operations are usually staggered enough to give a sufficiently uniform steam supply to avoid any serious irregularities in the demand upon the main boiler installation. Where the electrolytic power is obtained by transmission this variable supply might cause undesirable fluctuations, but in this case most of the steam would be used for heating purposes where considerable variations are temporarily permissible. On Sundays the waste heat steam supply is lessened but so is the miscellaneous demand.

A good general discussion of the whole question of waste heat boiler equipment has been given in a paper by Arthur D. Pratt,[1] and of the particular application to copper refining furnaces in an article by Clarence L. Brower.[2] The secret of successful operation lies in placing the boiler as close as possible to the furnace throat and in the exclusion of air infiltration. A good modern installation obtains a temperature of 1600° to 1700°F. in the boiler fire-box as against 1000° to 1200° in the earlier attempts. The exit gases may be brought down to 500°F. or lower.

Electrolytic Power.—As has been discussed in Chapter IV, the power required in the tank house depends upon the current density and the temperature of the electrolyte. In average practice the density will be around 18 amperes per square foot and the temperature about 130°F., in which case the power consumption will approximate 350 kw.-hr. per ton of copper deposited. In general a refinery with a capacity of 100,000 tons a year may be considered large enough to be a thoroughly economical unit and this would call for a dependable power capacity of about 4000 kw. Whatever type of steam driven prime mover be adopted, a thoroughly modern power plant of this size should deliver a kilowatt-hour at the switchboard for not over 15 lb. of steam, given reasonable superheat and vacuum and excluding auxiliaries. We, therefore, require at the throttle roughly 2.6 lb. of steam per pound of copper refined, or nearly double the 1.5 lb. available from the waste heat boilers.

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[1] *Trans.* A. S. M. E., vol. 38, p. 599.

[2] E. & M. J., vol. 99, p. 892.

Choice of Prime Mover.—In cases where water power is cheaper than steam at the place where a refinery has been located, generally for reasons quite apart from the cost of power, it is of course employed and we have such a case in the refinery at Great Falls, Montana. In the same way transmitted power originating at a water power is used at Tacoma and to a certain extent at Baltimore. A very unusual instance of power transmitted from a steam generating plant is that of the electrolytic department of the leaching plant at Chuquicamata, Chile. In general a refinery is located with reference to copper freights rather than cost of power and in most locations steam power is cheaper than water power.

Gas power has also been more or less discussed but up to the present time nowhere applied to copper refining work as far as power generation is concerned. The great first cost of the installation and its low economy at partial loads have always been handicaps. The history of refineries has been that they are continually being added to and expanded and that even individual units are seldom operated under the conditions for which they were designed, while above all else a gas plant lacks elasticity. On a basis of thermal efficiency some very interesting figures may be worked up, but very large steam turbine units can now practically equal these.

As between steam turbines and reciprocating engines, the question is largely a question of size of unit. A turbine can expand steam down to the highest attainable vacuum without unreasonable increase in size and owing to its high rotative speed very large units can be built in small compass. In the case of a reciprocating engine the speed is limited by valve gear considerations while cylinders larger in diameter than 54 in. are undesirable and the practical limit of size is about 72 in. diameter by 72 in. stroke. The low pressure cylinder is frequently divided into two in making a four cylinder triple expansion unit. These considerations bring us to about 2000 horse-power discharging into 27½ in. vacuum as a reasonable limit to size of unit for a reciprocating engine and the steam economy attainable is indicated in Fig. 35. A turbine of this size can hardly equal this performance even with higher vacuum and when the efficiencies of conversion from alternating to direct current are included it is under a serious handicap insofar as economy of steam consumption is concerned. In larger sizes, however, the turbine reaches very high economy. Figure 36 shows approximately what water rate may be expected with 170 lb. gage pressure, 150°F. superheat, 28½ in. vacuum after allowing 7 per cent loss for a.c.-d.c. conversion.[1]

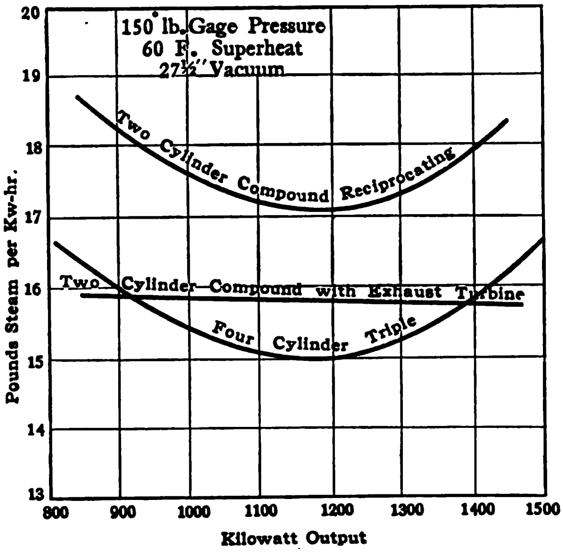

FIG. 35.—Water rate of 1200 KW. unit.

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[1] *Trans.* A. I. E. E., vol. xxxiii, p. 1133.

The advantages of a turbine are based partly upon its compactness and its ability to utilize high superheat and vacuum. One inch of vacuum or 50°F. superheat will vary the water rate five or six per cent in a high pressure turbine. As to the space factor it must be remembered that its value is considerably less at a refinery than in a city power house and regarding condensation the cost of producing high vacuum must not be lost sight of. The temperature of saturated steam drops very rapidly as vacuum increases and if cold water is not available the cost of circulating water may become very great. These conditions are illustrated by the curves in Fig. 37.

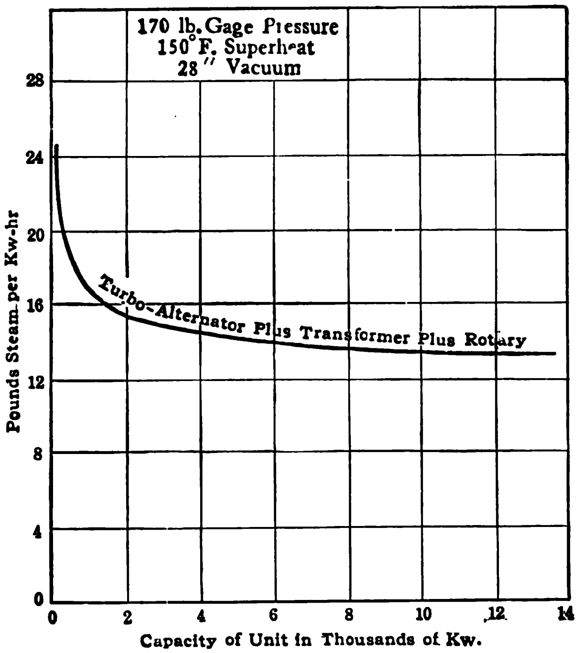

Fig. 36.—Steam turbine water rates.

The whole question of the relative value of the several types of prime mover has been reviewed by Stott, Pigott and Gorsuch,[1] and the special application to electrolytic work was discussed at a joint meeting of three of the engineering societies several years ago.[1] In a general way it can be stated that with cheap coal the plant will be steam driven, using reciprocating engines if small and turbo-alternators distributing through rotary converters if large. With expensive coal, a fairly large plant and regular tonnage a gas plant could be made to pay. With water power close at hand it would probably displace either steam or gas.

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[1] *Trans.* A. I. E. E., vol. xxxiii, p. 1133.

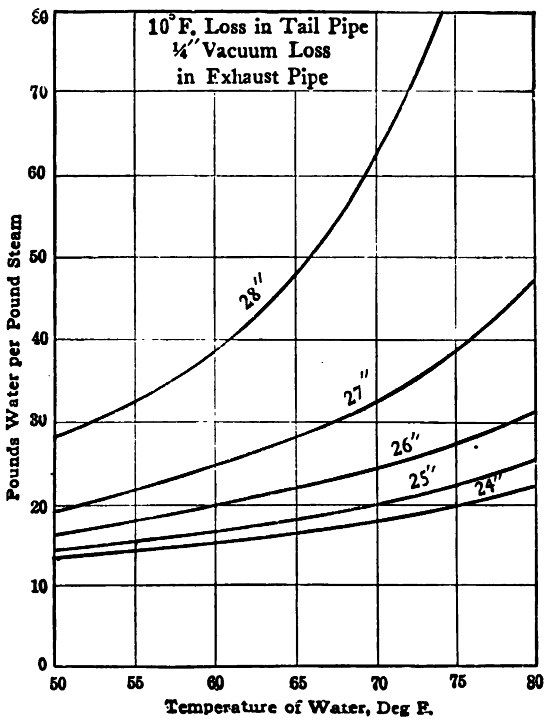

FIG. 37.—Water required for condensing.

The Electric Generator.—The tank house circuits demand (*a*) direct current, (*b*) high amperage, (*c*) low voltage and (*d*) wide voltage range. The amperage used has steadily increased as the generator builders have found it possible to build larger capacity commutators and to-day runs between 10,000 and 15,000 amp. per circuit.

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[1] Newbury, *Trans.* A. I. E. E., vol. xxxiii, p. 1; Longwell, *Jour.* A. S. M. E., July, 1914; Addicks, *Trans.* A. E. S., vol. xxv, p. 65.

The voltage is generally limited to 200 volts or less per circuit and the maximum unit to be considered is, therefore, 3000 kw., while 10,000 amp. at 120 volts or 1200 kw. would more nearly represent present practice. A 1,200-kw. generator, direct connected to a reciprocating engine, would call for 1,900 i.h.p., which is about the limiting engine size.

The generator problem is almost wholly one of commutation. This subject has been reviewed at length under the heading of "Physical Limitations in D.C. Commutating Machinery" by B. G. Lamme.[1] The simplest case is that of the direct connected reciprocating engine. Here the slow engine speed, certainly not over 125 r.p.m., permits reasonable freedom in commutator design, and the volts per segment, length of bar and amperes per brush arm can all be placed at conservative figures. It must be remembered that steady duty at 100 per cent current load and occasionally at abnormally low voltages imposes commutating conditions far more severe than met with in average practice and that any roughening of the commutator surface becomes rapidly worse. Commutating pole field construction has made a great advance toward sparkless commutation in all electrolytic generators.

The efficiency of a direct connected engine type generator exclusive of bearing friction will be about 94 per cent and the e.h.p. delivered by the generator should be about 88 per cent of the i.h.p. of the engine. The total losses on a 750-kw. C-W. generator built in 1905 are given in Table 48.

The direct current steam turbine has also given satisfaction in service, although there is a practical limit to the size of commutator which can be constructed, as it is necessary to restrict the diameter owing to the high rotative speeds required. A two cylinder compound driving a direct connected generator and exhausting into a direct current turbine connected electrically in parallel makes a satisfactory unit and several such pairs are in successful operation. The

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[1] *Trans.* A. I. E. E., vol. xxxiv, p. 1739.

TABLE 48

Voltage, volts	125	125	100
Current, amperes	0	6,000	9,500
Output, kw.	0	750	950
Bearing friction, watts	4,000	4,000	4,000
Windage, watts	1,600	1,600	1,600
Brush friction, watts	6,200	6,200	6,200
Core and pole losses, watts	18,000	18,500	15,000
Field copper, watts	6,560	7,930	4,680
Armature copper, watts	......	11,750	29,400
Brush resistance losses, watts	......	8,650	15,400
Total losses, watts	36,360	58,630	76,280
Mechanical losses, per cent input	32.4	1.5	1.1
Magnetic losses, per cent input	49.4	2.3	1.5
Electrical losses, per cent input	18.2	3.5	5.0
Output (efficiency), per cent input	0.0	92.7	92.4
Load, per cent rating	0.0	100.0	127.0

steam economies possible with such combinations are indicated in Fig. 35. This same field is covered by geared units, a rather high-speed generator being geared to a rather low-speed turbine. For large plants electrical rather than mechanical connection between turbine and generator, as provided by rotaries has many advantages.

The unipolar generator which delivers direct current without a commutator and which may be driven at turbine speeds is a very pretty theoretical solution of the whole problem. Practically, while commercial units have been built[1] many special problems are involved in the collection of the current and this type of apparatus has not received any considerable application.

If a turbo alternator is used as the main source of current allowance must be made for the efficiency of the distributing system, the transformers, conductors and rotary converters absorbing about 7 per cent of the A.C. output.

The voltage regulation should be made wide and is satisfactorily accomplished by hand control. In the case of reciprocating engines the speed may be altered so as to keep the engine operating at the best cut-off. This, however, means some adjustable attachment to the engine governor which has its draw-backs. With ordinary direct current generators, either engine or motor driven, the usual hand rheostat gives satisfactory voltage control and modern commutating pole generators will operate well at surprisingly low voltages. In the case of rotary converters it is necessary to use booster control on the alternating current side, which may be supplemented by employing multi-tap transformers.

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[1] Lamme, Transaction A. I. E. E., vol. XXXI, p. 1811.

A circuit of 120 volts would probably have 360 tanks connected in series and when drawing copper two groups of say 36 tanks each might be cut out. This would call for a 20 per cent cut in the normal operating voltage during this period. On the other hand while a tank house is supposed to be operated on a constant current basis, this is very apt to become constant wattage, the current density being temporarily increased during periods of low voltage.

Heating Electrolyte. Heating the electrolyte has already been discussed in Chapter IV. At what temperature it will pay to carry the liquor must be determined for each case. Eastern refineries expend about 0.75 lb. of steam per pound of copper produced to raise this temperature say 30°F. above the temperature which would result from electrical heating. This means a power saving at the generator of 15 per cent, taking an overall temperature coefficient of 0.5 per cent per degree Fahrenheit. If we are using 3.0 lb. of steam (including auxiliaries) per pound of copper at the engines the saving will be 0.45 lb. as against 0.75 lb. required at the heating coils and it is evident that live steam heating would not pay. If we run an electrolytic unit non-condensing it will take about 4.0 lb. of steam instead of 3.0. If we are able to run a proper proportion of the circuits non-condensing we can, therefore, furnish steam for heating the tanks and obtain an average overall steam rate of 3.2 lb. on 85 per cent of the original resistance or 2.7 lb. per lb. of copper instead of 3.0 when running without heating.

Where the electrolytic power is hydraulic live steam heating may not pay if there is not waste heat boiler capacity in excess of other needs, but except where very high densities are employed, thereby predicating clean bullion and resulting in considerable electrical heat being generated in the tanks, it generally is desirable to heat the electrolyte from purely metallurgical considerations.

The condensate from heating coils is generally collected for use in washing the anodes and cathodes free from slimes, bluestone crystals, etc., and a small amount of heat is in this way returned to the system as well as a safeguard established against leaky heating coils withdrawing any electrolyte and sending it to the sewer.

Boiling Tanks.—The silver refinery and the purifying system or bluestone plant will always require a certain amount of boiling or evaporating This varies greatly in amount in different plants. In a very general way it may be stated that there will be two pounds of steam condensed for every pound of water evaporated and that about 10 per cent of the total steam used will be employed in this way in the average plant.

Steam siphons used for pumping are really heaters, their efficiency as pumps running but a few hundredths of one per cent. The steam consumption of a siphon depends upon the original design and upon the amount of nozzle wear at the time of test, but one per cent dilution of the liquor pumped is probable and three per cent possible.

Heating Feed Water.—The steady full load conditions of the electrolytic engines call for a complete installation of economizers. Probably ten per cent of the steam furnished by the boilers will be called for as exhaust steam for further heating of the feedwater.

Miscellaneous Demand.—There is a considerable amount of pumping to be done, such as circulating electrolyte, circulating bosh water, supplying condensers, fire system, general water supply, feeding boilers and high pressure system for hydraulic cylinders. There is a more or less extensive compressed air system for operating copper hoists and pneumatic tools. There is power required for the motor drives of cranes, shop tools, ventilating fans, sampling drills and possibly an electric railway. Finally there is the lighting system.

If steam driven, non-condensing, in a large plant, these various units will consume from one-third to one-half as much steam as is called for by the electrolytic generators operated condensing. This steam may advantageously be turned into the heating systems, the requirements of which it roughly fills, turning all of the steam from electrolytic units into the condenser. Another solution is to electric drive all auxiliaries, supply the current by means of a non-condensing light and power unit. There is even the opportunity of utilizing an electrolytic spare for this service, thereby reducing the total equipment called for, the plant consisting of several electrolytic generators, one light and power unit and one spare for both services.

Summary.—The total steam consumption of a copper refinery will vary within wide limits, depending upon the size of plant, the current density employed and the amount of purifying of the electrolyte required and may be stated somewhat as in Table 49.

TABLE 49

	Lb. steam per lb. copper
A. Electrolytic power, condensing	2.5 to 3.0
B. Light, power, water, air and auxiliaries, non-condensing	1.0 to 1.5
C. Evaporating, live steam	0.5 to 2.0
D. Heating, exhaust steam	1.0 to 1.5
E. Total steam demand, $A + B + C + D$	5.0 to 8.0
F. Exhaust steam for D from B	1.0 to 1.5
G. Contributed by waste heat boilers	1.5 to 1.5
H. Net steam demand, $E - (F + G)$	2.5 to 5.0

CHAPTER XII

ELEMENTS OF DESIGN

Up to the present time electrolytic refining has been conducted almost exclusively in the United States, some eighty per cent of the world's production being there treated. This has been due to several factors. The North American continent has produced the great bulk of the world's output of copper, metallurgical operations have been developed on a larger scale in America than elsewhere and the local copper production has been largely consolidated into a few large groups each capable of supporting one or more large refineries.

Location.—Since the war the nations of Europe have developed a new desire to control key industries complete within their own borders, home or colonial, and new tariffs, trade routes, etc., are likely to cause the building of various new refineries. In general the factors associated with the movement of copper from mine to market, rather than those directly connected with refining, such as cost of power, are likely to control the location of a plant. Unless a plant is built to refine a large tonnage from a single group of mines, care must be taken when determining upon its location to consider breadth of both copper supply and market. The result has been to group a number of the American refineries around the port of New York, because at that point rail shipments from Western Smelters and ocean arrivals fom South America conveniently join steamship deliveries to Europe and railroads to New England mills. One of the advantages of having a refinery close to an Atlantic port is that orders can be promptly filled in the particular shape specified, enabling the European customer to play close to a fluctuating market which at times would result in a preferential sale. Another objection to locating a refinery at a far distant mine is that a long time elapses between the production of a wirebar and its actual rolling, so that there is no prompt independent check upon the quality of product the plant is turning out. Aside from these considerations, the availability of a suitable coal for furnace work and the existence of a good boiler water together with ample water for condensing must be looked into.

Capacity.—In the same way external considerations may justify the operation of a plant of a capacity far below the economic size, but the latter is a point of universal interest.

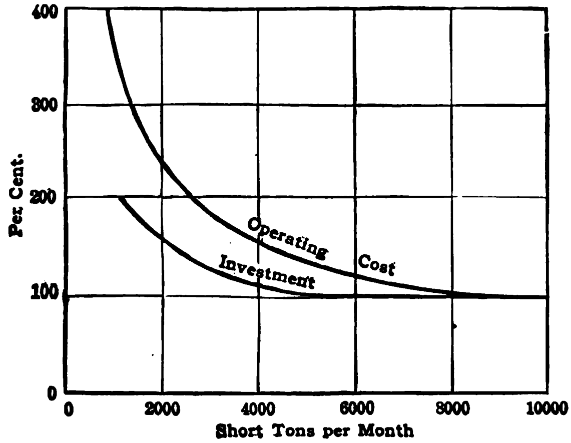

FIG. 38.—Variation of cost with size of plant.

In these days of economic disturbance it is very hard to state anything in terms of absolute cost, but a relative diagram may be made, showing with reasonable reliability the relation between plant capacity and operating cost. This has been attempted on a percentage basis in figure 38, where it is shown that not much is to be gained, insofar as cost is concerned, by making a plant of larger capacity than 200,000,000 lb. of copper per year. Even this figure, however, is beyond the reach of any but the largest mining groups so that there will always be a large custom refining business.

Tank House.—Having decided upon the size of plant to be constructed, the next problem is the choice of the current density. This question has already been discussed at length in Chapter IV, and in turn depends upon several primary factors such as cost of power, silver values, etc. It has also to be remembered that the plant will earn more interest on its investment when operated at a little higher density than that giving the lowest operating cost, as shown on page 69. On the other hand, it is generally wise to leave this margin for the growth of the business.

The density having been settled upon, tank dimensions have next to be considered. In the earlier plants electrodes about 2 ft. × 3 ft., twenty pairs to the tank, were used with densities around 15 amp. per square foot. This gave 3,600 amp. on a circuit which was in those days a heavy amperage to rectify on a single commutator. To-day 30 pairs of electrodes are used without material lowering of the current efficiency and in one plant electrodes 4 ft. square are in successful use, although 3 ft. square is a more popular size where soluble anodes are employed. With 30 pairs of 3 ft. electrodes and the average density of 20 amp. per square foot, the current on a circuit becomes 10,800 amp., still well within the limits of the modern commutator. At an overall current and time efficiency of 85 per cent, this current will produce 17,258 lb. of copper per tank per month, or 575 lb. per pair of electrodes.

The spacing center to center of anodes will lie between 4 and 4½ in., depending upon the purity of the bullion treated and the age of electrodes adopted. In general the column of liquor between anode and cathode should be about 1¼ in. across. General practice as to the age ratios of electrodes is indicated in Fig. 39. At the lower densities cathodes and anodes are of identical age while as the density rises increasing numbers of sets of cathodes are drawn during the life of one set of anodes. The weight of the anode can be obtained by multiplying the expected output per tank-day per pair of electrodes by the days life determined upon and adding 15 per cent to this figure to allow for anode scrap. From the area and weight (allowing something for porosity) the thickness may be calculated and this plus 2½ in. will give the anode spacing.

Having settled upon the output per tank-day, the total number of tanks required is at once obtained and the next question to be considered is the number of independent circuits required. In general the voltage per tank will be somewhere btween 0.30 and 0.45 volt. This figure depends upon many factors, the chief being the current density.

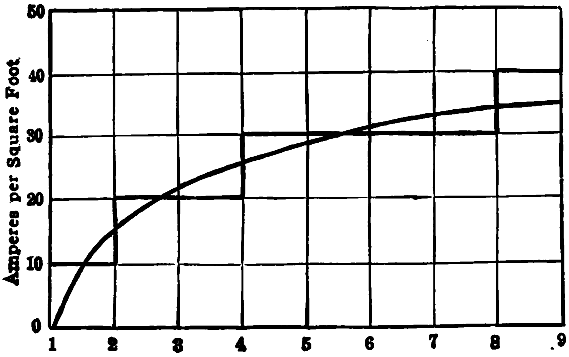

FIG. 39.—Crops of cathodes during life of anode.

An average value in practice would be 0.35 volt. To this must be added a sufficient allowance for liberator and stripper tanks. The liberators require about 2.2 volts when on normal work and 2.5 volts when used for complete removal of copper. Ordinary work would call for 2 per cent of the former and none of the latter, but this depends upon the analysis of the anodes to be handled. Stripper tanks are operated on a somewhat wider spacing than regular tanks and this means fewer pairs of electrodes, higher current density and higher voltage—say 0.50 volt as compared with 0.35. If we take 80 per cent of the number of electrodes per tank, 24-hr. sheets, allow another 20 per cent for loops and bad production and 10-day cathodes, not forgetting that one stripper blank yields two starting sheets, each regular tank will demand the equivalent of

3 sheets a day while each stripper tank will produce 38 sheets a day.

Power House.—The general power problem was reviewed in the last chapter. To this may be added, however, some notes on electrolytic switchboards.

Heavy direct currents are satisfactorily handled by multiblade knife switches with a duty of 50 amp. per square-inch of sliding contact. Circuits are neither opened nor closed under load but a circuit breaker with a no-voltage release should be placed on each circuit, not as a protection to the generator, the armature resistance of which is too low to "short circuit," but to protect men and apparatus in the tank house. It is not uncommon to have an open circuit due to the crane drawing cathodes by mistake from a tank which has not been cut out and heavy arcing may result. A bar or tool laid across lines where any considerable effective voltage is present is promptly "burned out." An automatic engine stop should also be provided in the case of reciprocating engines as with a sudden release of load due to the opening of the circuit breaker there is always a chance that the governor will act sluggishly, as the steady full load day after day gives it but little exercise.

Recording and integrating instruments are not of great value on the electrolytic switchboard, beyond giving a check on the employes, as hourly readings of the indicating instruments are ample for all records.

Several precautions are necessary in setting instruments on the board.[1]

With voltmeters there is little trouble, though the same precautions must be taken with regard to the effect of stray field as stated below for ammeters. The very heavy currents met with in electrolytic work accentuate some causes of error which are ordinarily negligible in switchboard ammeters, and if a limiting error of 1 per cent is to be attained, distribution of the current in the shunt, thermoelectric effects, switchboard temperature, the magnetic effect of stray field on the instrument and possible dynamo action of the leads, must be accounted for. One per cent error may be taken as the limit of accuracy of the best types of switchboard ammeters for heavy direct current.

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[1] Addicks, *Trans.* Am. Electrochemical Society, vol. 8, p. 239.

Care should be taken to place both shunt and instrument in suitable positions when designing the switchboard. In the first place the shunt should be obtained from the maker with short bars inserted in the slots usually provided in the shunt terminals, these bars in turn to be bolted to the bus bar carrying the current to be measured. In this way the shunt is calibrated with the same distribution of current through the various leaves, as will be the case in after use. It is practically impossible to disconnect a high capacity shunt down to the slotted terminals and put it back in place again without altering the calibration more or less, due to change in the distribution of the contact resistance between main bar and shunt terminals, and consequent slight change in the amount of current carried by the different leaves of alloy. This, in turn, slightly affects the ratio between drop of potential between binding posts and total current carried. These changes in resistance are very small, but the total resistance of a good 5,000 amp. shunt is but about 0.00001 ohm. There is no way to detect the error introduced in this way except by calibration in place.

Unequal heating of the two shunt terminals will introduce a constant error from the thermo-electric junctions formed where the alloy leaves are soldered on to the copper blocks. This may easily amount to 1 per cent of the full scale reading, may be either positive or negative, and will show as a zero error on shutting down the circuit which will gradually disappear as the shunt cools off. Sometimes compensating devices are applied to avoid thermoelectric errors, but if the shunt is so placed in the bus bar that the facilities for conducting away heat are approximately equal on both sides, there will be no appreciable error, and such devices should be unnecessary. The alloy leaves of a shunt would be red-hot at full load were it not for the heat dissipating qualities of the large copper terminals. There should be practically equal radiating surfaces of bus bar for three or four feet each side of the shunt. If placed close to a switch on one side, there is sure to be a thermoelectric error in the shunt, as high capacity switches frequently run hot. The best plan is not to attempt to place the shunt back of the switchboard at all.

The temperature at which a shunt runs will depend upon how heavily it is loaded and the opportunity afforded to dissipate the heat generated. The temperature indicated by a thermometer and well placed upon one of the terminal blocks should not be allowed to exceed 200°F., owing to the danger of starting the solder and consequent failure. The temperature coefficient of the alloy used in the resistance leaves is generally so low that no correction to the instrument reading need be applied for the heating of the shunt.

A sensitive millivolt meter is used to measure the drop. The condition for maximum sensitiveness would require that all of the resistance of the instrument be in the armature of the d'Arsonval type so generally used. And in order that a given resistance may afford as many ampere turns as possible without making too heavy a bobbin, the material must be one low in specific resistance, such as copper. The use of copper means a high temperature coefficient, and in order to keep within 1 per cent on large switchboard ammeters it is always necessary to correct for instrument temperature. The largest size of instrument —independent of capacity, as change of size for current rating is made in shunt and not in instrument—has a temperature coefficient corresponding to that of pure copper, or 0.24 per cent per degree Fahrenheit. The smaller types are lower in temperature coefficient, as the lighter movement gives the instrument designer more leeway. In high resistance instruments, such as voltmeters there is a series coil, made of low temperature coefficient alloy, which forms so large a proportion of the total instrument resistance that the coefficient of the whole is negligible.

One of the most important sources of error is the magnetic effect of stray field in the immediate vicinity of a bar carrying several thousand amperes. Instruments should never be placed within two feet of such bars. The iron shield usually provided is not only likely to be faulty as a filter for lines of force of such density, but consequent poles are formed in the case itself.

The magnet of an unscreened Weston portable instrument may be permanently altered by placing the meter too close to such a bar, and this is very easy to do, especially in the tank house. Even at a distance of several feet the readings of a portable instrument are thrown out a division or two on the scale and where accuracy is desired the average of two readings with the instrument turned 180 deg. should be used.

The resistance of the leads on a switchboard ammeter is generally some 5 per cent of that of the instrument, and the screw connections must be kept clean. If it is found necessary to lengthen the leads, care must be taken that the resistance is kept constant by a proportionate increase in size of wire used. The leads should be twisted and kept from swinging loosely in the presence of stray field. Otherwise there is a dynamo action which the millivoltmeter is sensitive enough to indicate by a pulsating needle.

When several high capacity ammeters are in use, it is advisable to have them interchangeable. The various instruments may then be checked at any time by connecting them to the same shunt. Connections should also be arranged, if possible, to put the shunts in series, when they too may be checked.

The question of proper section for bus bars has been discussed on page 43. No insulation is used and faced metal to metal joints without amalgam, tightly bolted together are satisfactory at 200 amperes per sq. in. contact surface. Either rolled or cast bars may be employed. The bars from the switchboard to the tanks are best carried overhead and the positive and negative leads kept some distance apart.

Furnaces.—For smooth operating there should be at least six furnaces, three anode and three wirebar units, two of each being in service and one out for repairs. For a capacity of 100,000 tons a year, and allowing for Sundays and holidays out, we should have 600 charges a year of 333,000 lb. each plus scrap, etc. which is a furnace of fair size, although it is possible to build them very much larger.

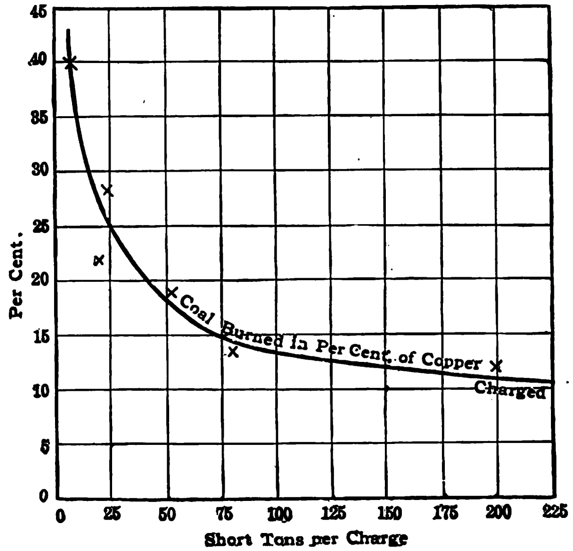

Fig. 40.—Fuel ratio of furnaces.

The limit of size has been the ability to charge, refine and cast the charge in twenty-four hours. With hand charging and ladling, using the same men for both operations, 60,000 lb. is a large furnace. If a fresh crew is used for charging and as many ladlers employed as can be accommodated at the ladle door, 100,000 lb. can be reached. With hand charging but mechanical ladling 300,000 lb. is possible, using three charging doors. With full mechanical charging and ladling 500,000 lb. is easily reached and using two charging and ladling machines even a larger capacity can be attained.

The fuel economy increases rapidly with the size of furnace as indicated by the curve in Fig. 40. Labor charges also fall up to the point of mere duplication of machine units. Repairs fall at first but a very large furnace is likely to incur heavier repairs than one somewhat smaller. This is especially true where too great a span of roof is attempted. A refining furnace is subjected to much greater and more rapid temperature changes than an ore reverberatory.

Small silica furnaces produce excessive slag as they run hot and have an undue proportion of wall exposure. A 40,000 lb. silica furnace will form 4 or 5 per cent of slag on a wirebar charge, whereas a similar furnace of 150,000 lb. or over to the charge can be held down to half that amount. With basic side walls there is a substantial decrease in these figures and with a full basic furnace operating on a charge of good quality the slag made can be held down to 0.5 per cent or better.

Altogether a furnace casting a charge of 300,000 lb. or more may be considered a thoroughly economical unit.

Silver Refinery.—A 100,000 ton plant will call for a silver refining department of reasonable size. At 1.25 per cent slimes there would be four tons of slimes a day to treat calling for a doré reverberatory of about 20 tons capacity, just the size of the first copper furnaces. It is desirable to use but a single furnace in order to hold at a minimum the large bottom absorption of values. A spare furnace may be held in reserve and in case of accident or at inventory time substituted, the first unit being completely dismantled at that time and its silver content recovered.

A very small plant can best sell its slimes to a lead refinery but owing to the difficulty in getting a fair sample of such rich material this is not desirable when the tonnage is of any size. Small plants would use a cupel furnace and sulphuric acid parting while reverberatory smelting followed by electrolytic parting is generally employed in large ones.

Where the purifying system affords a suitable outlet for accumulations of sodium salts in the electrolyte niter may be used to remove the copper from the slimes. Where closed cycle operation is undertaken the copper is generally oxidized by roasting. Either method gives good metallurgical results.

Purifying.—The metallurgical principles upon which the choice of a purifying system must be based were taken up in Chapter VI.

Where insoluble anode tanks are employed for the complete removal of the copper from batches of electrolyte, ample provision must be made for the very low current efficiency of these tanks. Should a bluestone plant be employed, the design will be based upon the quantity of shipping salt to be produced. The crystallizing tank space employed in different plants varies considerably. A fair average figure, making allowance for the recrystallization of fines, is 58 cu. ft. per short ton per month of marketable bluestone. When estimating the proportion of impurities removed from the electrolyte it must be remembered that a large part of the copper in the bluestone comes from the shot towers and not from the electrolyte. For each 1000 cu. ft. of crystallizing space, allowance should be made for say 175 cu. ft. shot towers, 375 cu. ft. shot tower receiving tanks, 225 cu. ft. slimes settling tanks, 250 cu. ft. boiling tanks, and 275 cu. ft. iron cementation tanks. These ratios, however, may be varied between rather wide limits to suit individual cases differing in analysis of electrolyte, character of shot, climate, etc.

General.—Two main principles should be kept in mind in the program of operation of any plant. The first is that all the impurities possible should be eliminated at the anode furnaces, using basic furnaces if necessary. It is much more costly to throw this burden upon the tank house and silver refinery.

The second is to do everything possible to facilitate uniformity of operating conditions. As a general rule anodes of constant composition, a uniform current density and a single electrolyte should be used throughout the tank house.

CHAPTER XIII

APPLICATION TO OTHER FIELDS

Electrolytic refining has attained its chief application and highest development in the metallurgy of copper. The very dynamo, the invention of which created the large-scale demand for high-conductivity copper, gave the means of producing it by electro-deposition, and electrolytic refining on a commercial scale was one of the first electrical industries to be developed, while it remains today by far the largest application of the electrolysis of an aqueous electrolyte.

The experience gained in this field has found wide application in the refining of other metals, such as silver, gold, lead, bismuth, tin, nickel, iron and zinc, and in the recovery direct from the ore by leaching of copper, silver, gold and zinc. The successful application of electrolysis to these different fields requires a rebalancing of the various factors discussed in the foregoing chapters, the relative values of which are often greatly altered by a change of metal. In any given case we must take into account (1) competition from other processes, (2) acid radical to be employed, (3) temperature of electrolyte, (4) character of deposit, (5) resolution at the cathode, and (6) depolarization at the anode.

Competition.—Electrolytic copper refining has no effective competitor in its own field. Fire refining makes a low conductivity product unless furnished with very pure raw material such as selected Lake "mineral," and the various selective methods of reverberatory treatment yield but a partial recovery of gold and silver.

In the leaching field electrolysis has to meet several competitive methods of reduction, notably precipitation upon iron. While a free acid equivalent by electrolyzing is returned to the cycle, there are usually serious handicaps imposed by large quantities of impurities which cause various troubles in the cells and which progressively accumulate unless some outlet is provided. Even where electrolysis is indicated, therefore, an iron precipitation plant is usually required as an adjunct, from 10 to 30 per cent of the copper being recovered as cement.

Electrolytic silver has to compete with the older sulphuric acid method of parting. The latter is easy to operate and ties up less silver, but it will not make a product so low in gold as the electrolytic. It is still indicated, however for small plants and for those which are used spasmodically.

In the case of gold refining the question is almost wholly dependent upon the amount of platinum and associated metals present. If the original gold is free from this metal group, there is no object in tieing up the gold several days for electrolysis and further increasing the opportunities for theft. When but very small quantities of platinum and palladium are present, they may be satisfactorily collected by wet methods instead of by electrolysis at about equal expense. When the qualities are larger electrolysis is indicated.

Electrolytic lead has to compete with the very efficient Parkes process of refining. When all factors are considered, the justification for electrolysis appears to rest almost entirely upon the quantity of bismuth present in the bullion to be treated. This objectionable impurity is not satisfactorily removed by the Parkes process and special treatments such as Pattisonizing are expensive, while the electrolytic method readily separates the bismuth from the lead and converts it into a marketable byproduct.

Nickel, iron and zinc may be readily refined by electrolysis, but in ordinary times the value of the refined product, except in a very limited quantity, is not sufficiently above that of the crude to pay for the refining. Tin offers a special field for impure ores which are difficult to handle by fire processes.

In leaching, both nickel and zinc have strong competition from chemical and pyrometallurgical processes and this whole field is still in a state of flux.

In general, we can say that electrolysis enjoys no such absolute monopoly in other fields as it does in copper refining and that each proposed application must, therefore, receive full consideration upon its merits.

Acid Radical.—While several salts of copper are suitable for electrolytic treatment, the sulphate possesses so many practical advantages that it is universally employed. The first requirement foı an electrolyte is that the salt of the metal employed shall be readily soluble. The second is that the material which it is desired to collect in the slime shall be insoluble in it. The third is that the cathode should not be redissolved by the electrolyte. Copper sulphate is a readily soluble salt and copper, gold and silver are all practically unattacked by dilute sulphuric acid.

When electrolyzing silver a nitrate electrolyte is employed, as silver sulphate is not a readily soluble salt. The amount of free acid carried is necessarily low, as nitric acid is expensive and decomposes under the conditions of electrolysis. Copper concentrates in the electrolyte and is removed by withdrawals, while gold remains unattacked in the slimes.

In gold refining a chloride electrolyte is employed. Gold chloride is a soluble salt, platinum concentrates in the electrolyte, and although silver, being less noble than gold, dissolves at the anode, after saturation it precipitates as a secondary slime of insoluble chloride.

For lead, chloride and acetate were first tried, but not until Betts developed the fluosilicate electrolyte was the electrolytic refining of lead made a commercial success.

It will, therefore, be appreciated that an entirely new set of chemical conditions as regards behavior of impurities, etc., is encountered with every metal refined.

Temperature of Electrolyte.—When it is customary to heat copper electrolytes externally, quite opposite conditions obtain in the case of silver, lead and zinc. Nitric and hydrofluosilicic acid show increasing decomposition losses with rise in temperature, asphalted tanks do not stand hot liquors and zinc resolution losses must be limited. In the case of silver, the current may have to be limited to control the temperature; for lead, extraneous heating is abandoned, and with zinc, where the specific resistance of the electrolyte is high, cooling systems carrying circulating water must be employed.

Character of Deposit.—At moderate densities copper readily gives a good adherent deposit. The same may be said of gold. Silver gives normally a loose crystalline deposit. Nickel is nodular, while lead and zinc tree very badly. By the proper use of addition agents all of these deposits may be made smooth and coherent. In fact it was not until the value of addition agents was more or less understood that lead could be handled at all.

In the early copper plants a great deal of trouble was had in getting good starting sheets, and it was thought that the addition of ammonium sulphate was a help, the use of double salts being common practice in various electroplating prescriptions. Then the beneficial effect of the presence of wood strips on the edges of the starting blanks led to the introduction of wood tea made from shavings, yielding a complex organic addition agent. Finally the remarkable results following the addition of gelatine were worked out. The irregularities of early practice were due to overdosing and a failure to appreciate the fleeting effect of a single dose. Today a few pounds of common glue dissolved in water and added regularly throughout the twenty-four hours, together with a can of ordinary engine oil, will control the deposit in the tank house of a great copper refinery, permitting the use of higher densities, closer spacing and greater cathode age.

For silver, while adherent deposits can be made in similar fashion, it is customary to collect the silver crystals as such, either brushed to the floor of the tank from vertical cathodes by mechanical scrapers as in the Moebius system or shoveled by hand from the horizontal carbon cathode of the Thum cell. These crystals are readily washed free of electrolyte and fed to retorts for melting.

Lead may be beautifully controlled by addition agents. The exact amount to be added varies from time to time and is determined by experiment and careful watching of the fresh deposit on special strips hung for the purpose.

Zinc is generally plated in coherent form on an aluminum cathode, from which it is peeled every forty-eight hours. There is no reason why zinc starting sheets could not be used as in the case of copper, and in some ways the avoidance of a zinc-aluminum couple would be of advantage. In the development of electrolytic zinc practice, however, there has been great difficulty in controlling resolution at the cathode, and the great advantage of using aluminum sheets lies in the fact that strong corrosion can do no more than leave the starting sheets bare, whereas were they of zinc they might be completely eaten through, causing collapse, open circuits, general demoralization and shutdown of the plant.

Resolution at Cathode.—The cathode is never absolutely insoluble in the electrolyte used and a small amount of reoxidation is always in process. In the case of copper with normal electrolytes it is a minor matter—perhaps 2 per cent. Should we allow an accumulation to take place of salts of manganese, iron or any other metal capable of alternate oxidation and reduction at anode and cathode with change of valence, a very serious condition may arise.

In these days copper anodes are so highly refined that the amount of iron contained in the electrolyte is quite negligible, but when electrolyzing liquors arising from the leaching of ore a very different situation exists. Such liquors commonly contain large quantities of ferrous sulphate and a certain proportion of ferric sulphate. Oxidation at the anode tends to increase the latter at the expense of the former.[1] Experiments show that 0.25 per cent of iron as ferric sulphate in an electrolyte sufficiently agitated will corrode cathode copper at a rate which will require a current corresponding to about 8 amperes per sq. ft. merely to replace the loss. The proper control of ferric sulphate is, therefore, the key to success in electrolyzing copper leaching liquors.

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[1] See Addicks, *Trans. Am. Electroch., Soc.*, vol. 28, p. 87.

Another interesting example of resolution is in the case of zinc—in fact this is the controlling factor in zinc electrolysis. In the electrolysis of zinc sulphate using an insoluble anode the content of free sulphuric acid gradually increases and unless the cathode is absolutely pure zinc resolution is very active. Perfectly pure zinc is so nearly insoluble in sulphuric acid that it is quite difficult to get it in solution for analysis. But if a nodule of cathode zinc is immersed in dilute sulphuric acid in a test tube and the merest trace of almost any impurity is added, a vigorous evolution of hydrogen will start at once. This is probably due to galvanic action, and the whole secret of successful zinc electrolysis lies in the passivity of pure zinc in sulphuric acid. This calls for a degree of purity in the electrolyte which would be quite uncommercial were it not for the fact that zinc dust readily throws down most of the impurities to be dealt with after the liquor from the leaching tanks has been neutralized. The last traces of some difficult elements, such as arsenic, are removed by adsorption upon freshly made ferric hydrate.

Depolarization at the Anode.—Anode efficiency plays a relatively small part in normal copper refining; the proportion of impurities present in the anode is small and the useful anode efficiency very high. As soon as a complex or insoluble anode is substituted, however, the oxidizing effect of the current is in part or in whole employed in the solution of anode impurities, the oxidation of suitable salts in the electrolyte or in the decomposition of water with escape of oxygen as such. This introduces several new problems.

A moderate amount of an oxidizable impurity, such as nickel, in a copper anode gives the first and simplest case. The nickel and copper dissolve proportionately at the anode, sharing the current. At the cathode, however, only copper is deposited, so that the copper in the electrolyte is correspondingly depleted. About 2 per cent of the copper deposited is restored by purely chemical solution at the electrodes but beyond that figure soluble copper must be added by leaching shot or scale, and the accumulating nickel must be controlled by withdrawals to a byproduct plant.

The second difficulty arises when the quantity and nature of the impurity in the anode causes segregation into two than the components one of which is more readily dissolved other. Then the anode disintegrates unevenly and a large amount of scrap has to be reworked.

A third and more serious condition is met with when the impurity is insoluble, such as lead or antimony, when the anode will become coated with a non-conducting slime. The voltage will then rise until some free oxygen is generated from the moisture underneath. This in turn will burst through the coating and the anode will act normally for a few seconds, when the coating will again form. A voltmeter connected across such a tank will show a wildly fluctuating needle, and this condition, known colloquially as "crazy tanks," is fatal to good refining, entailing as it does excessive gold and silver losses in the cathode, high power cost and a heavy expense for purifying electrolyte. The remedy lies in properly refining the crude material before casting the anodes.

Finally, we have the extreme case where the anode is by intent insoluble, as where copper is being recovered from leaching liquor. Where no depolarizer is employed, the voltage must of course be sufficiently high to decompose water, and free oxygen is given off at the anode. When the liquor is virtually free from chlorides and nitrates, antimonial lead is generally used as the anode material; when electrolyzing zinc, however, pure lead is required in order not to poison the cathode with specks of antimony. When the liquor is corrosive, either magnetite or one of the ferro-alloys, generally ferro-silicon, is employed. None of these anode materials is wholly free from oxygen attack.

Lead peroxidizes and sulphatizes and the iron alloys slowly dissolve, so that a certain replacement charge must be reckoned with.

Where an efficient depolarizer is employed, any of the materials mentioned above or carbon may be employed. Graphite offers peculiar advantages in that 100 per cent of efficiency of oxidation of ferrous sulphate or similar depolarizer is readily obtained by its use. Lead does not give equal results. On the other hand, carbon itself will oxidize and disintegrate if not fully protected by the depolarizer. This whole question of a cyclic oxidization at the anode with subsequent reduction at the ore contact is yet in but partially developed form, most of the theoretical advantages being generally offset in practice by the difficulties met with in handling impurities dissolved from the ore.

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